Structural Analysis of Planar sp$^3$ and sp$^2$ Films: Diamond-Like Carbon and Graphene Overlayers

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ABSTRACT

Structural analysis of planar sp³ and sp² films: Diamond-like carbon and graphene overlayers

Ahmed E. Mansour

The special electronic configuration of carbon enables the existence of wide ranging allotropes taking all possible dimensionalities. The allotropes of carbon are characterized by the type of hybridized bonding forming its structure, ranging from pure sp² as in graphene, carbon nanotubes and fullerenes, to pure sp³ as in diamond. Amorphous and diamond-like carbon consists of a mixture of both hybridizations. This variation in hybridization in carbon materials enables a wide spectrum of properties, ranging from high bulk mechanical hardness, tribological properties and chemical inertness made possible by moving towards pure sp³ bonding to the extraordinary electrical conductivity, optical properties and in-plane mechanical strength resulting from pure sp² bonding.

Two allotropes at the extremes of this spectrum, diamond like carbon (DLC) and graphene, are investigated in this thesis; the former is investigated as a protective coating in hard drive applications, while the latter is investigated in the context of chemically derived graphene as material for transparent conducting electrode applications.

DLC thin films are a main component in computer hard drives, acting as a protective coating against corrosion and mechanical wear of the magnetic layer and read-write head. The thickness of DLC films greatly affects the storage density in such devices, as larger separation between the read/write head and the magnetic layer decreases the storage density. A targeted DLC thickness of 2 nm would increase the storage density towards 1 Tbits/inch². However, difficulty achieving continuous films at such thicknesses by commonly used sputtering methods challenges the industry to investigate alternative methods. Filtered cathodic vacuum arc (FCVA) has been proposed as an efficient technique to provide continuous, smooth and ultra-thin DLC films. We investigate the influence of deposition angle, deposition time, and substrate biasing to define the optimum process window to obtain smooth and sp³-rich DLC films on model Si substrates.

Graphene has attracted worldwide attention since its recent discovery in 2004, due to its
extraordinary properties. One of the most promising applications of graphene is its use as a transparent conducting electrode in photovoltaic and display applications. Unfortunately, large scale deposition of graphene is still a challenge and a limiting factor. Solution processing of graphene oxide, a type of chemically derived graphene that forms well dispersed single sheet solutions, is an easy method of depositing large scale graphene films. Subsequent reduction allows recovering part of the properties of graphene. However, residual defects and oxide groups remain in the sheet even after optimal reduction processes, making it difficult to achieve the extraordinary electrical and transport properties of graphene. We investigate the structural, chemical, and morphological implications of plasma oxidation of CVD graphene to better understand the nature of graphene oxide.

One of the common threads of this study is the use of Raman spectroscopy (RS) X-ray photoelectron spectroscopy (XPS), and Atomic force microscopy (AFM) to understand the structural and compositional changes of both FCVA-deposited DLC films and plasma-oxidized graphene. In both cases, the analysis allows to obtain detailed insight into structural evolution of sp\(^3\) and sp\(^2\)-rich films during plasma processing.

Optimum FCVA deposited DLC films were obtained at a deposition angle of 70° for 30 sec deposition time on a biased substrate (-100 V), in terms of both surface roughness and sp\(^3\) content. RMS roughness of deposited films were around 0.15 nm with a ~50% sp\(^3\) content.

Structural and chemical changes of oxygen plasma treated CVD graphene were shown to vary over three distinct stages depending on the time of plasma exposure. Initial exposure up to 3 seconds was mainly accompanied by structural changes without net uptake of oxygen, introducing more defects and smaller crystallite size into the graphene sheet. Extended exposure resulted in a nano-crystalline structure with a crystallite size of around 4 nm with a significant uptake of oxygen. Significant degree of disorder and loss of materials were eventually observed at exposure times larger than 10 s. A three stage model of graphene oxidation was suggested summing up the observed variations.
ACKNOWLEDGEMENTS

Two years ago, the journey of pulling this work into existence has started with faith and determination to reach the finish line with a satisfying sense of accomplishment. Many challenges and difficulties have been faced along this journey; however, harsh conditions make the best of an effort, similar to carbon which transforms to diamond under high pressure and temperature.

Here I am two years later, presenting this work proudly and looking at a fruitful tree which was seeded with continuous hard work and support with this master’s thesis as the final crop.

It wouldn’t have been possible without God’s blessings and my parent’s prayers and support. I would like to express my deepest sense of gratitude to my supervisor Dr. Aram Amassian for his support and advice throughout this project in both the experimental work and writing this thesis. I acknowledge the efforts of the post-docs in our research group for assisting me in developing my expertise and knowledge in this project; Dr. HadayaUllah Khan, Dr. Ruipeng Li and Dr. Kui Zhao. Specials thanks to KAUST’s core lab researchers for training and support on various characterization tools used in this project.

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Chapter I

Introduction
1.1 - Carbon: Structure, properties and applications

Carbon is believed to be the basis of life; being one of the most abundant elements in earth's crust and the universe, as well as the second most abundant element in the human body after oxygen. Millions of compounds around us are composed of carbon, and have taken their place in every aspect of human civilizations throughout history, forming the main construction material in the form of wood which consists of lignocelluloses which is a biopolymer of hydrocarbons. The stability of carbon in forming the backbone of long chains of molecules has driven the science of polymers to deliver various products serving our everyday's life such as plastics, adhesives and rubbers. Small molecules and oligomers have been used in pharmaceuticals, besides the role hydrocarbons play in energy economy.

Carbon occurs naturally in several forms having different physical properties; it exists in the form of diamond, graphite and amorphous carbon. In recent decades, many more of its allotropes have been reported, starting with the discovery of the buckminsterfullerene (zero-dimensional “0D”) in 1985, which is a hollow spherical molecule formed by a stable network of at least 60 carbon atoms, followed by the discovery of hollow cylindrical carbon molecules (one-dimensional “1D”) also known as carbon nanotubes in 1991, and finally in 2004 single graphene sheets (two-dimensional “2D”) were isolated. These allotropes, ranging from diamond and amorphous carbon to fullerenes, cover all possible dimensionalities of materials from 3D down to 0D, a feature that hasn’t been observed for any element other than carbon.

The wide diversity of carbon compounds and allotropes is enabled by its electronic configuration and ability to assume different types of bonding arrangements. Carbon is located in the 6th group of the periodic table, giving it 4 valence electrons free to bond covalently with other elements. Two of these are in an S-orbital while the other two are in P-orbitals, thus yielding the ground state electronic configuration of \(1s^2\ 2s^2\ 2p^2\ 2p^1\), as shown in Figure 1.1. Carbon’s ability to form many allotropes and compounds relies on the orbitals’ hybridization which results in different forms of bonding.
Hybridization can generally result in two types of covalent bonds around the atom; sigma (σ) bonds which are strong covalent bonds formed through overlapping electron clouds around the nuclei, and the π bonds between overlapping P-orbitals, which are weaker bonds formed by delocalized electrons.

When two carbon atoms approach one another, one of the electrons in the S-orbital is excited into the P-orbital forming the configuration of 1s² 2s¹ 2pₓ¹ 2pᵧ¹ 2pᶻ¹, thus leading to hybridizations. Three types of hybridizations are possible depending on whether the S-orbital is mixed with one, two or three P-orbitals.

![Figure 1.1: Electronic configuration of carbon atom in ground state](image)

Mixing the S-orbital with the three P-orbitals results in four strong σ-bonds known as sp³ hybridized bonds as shown in Figure 1.2a. These bonds rearrange in a tetrahedral geometry with an internal angle of 109.5°, and are responsible for the structure of diamond. Hybridization of the S-orbital with two P-orbitals results in formation of three strong σ-bonds in one plane and a weaker π-bond orthogonal to the plane of σ-bonds. The three sigma bonds, known as sp² hybridized bonds, are coplanar and are arranged in a trigonal geometry with a separation angle of 120°, as shown in the case of graphite in Figure 1.2b. Graphite is composed of stacked graphene sheets via orthogonal π-bonds. Amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C), on the other hand, consist of a combination of sp³ and sp² hybridized bonds within their disordered structures.
This diverse bonding configuration provides the wide spectrum of properties and applications reported for carbon materials, as shown in Figure 1.3. The sp\(^3\) hybridization is responsible for the exceptional mechanical hardness in all three dimensions, tribological properties and electrical insulation observed in diamond and a-C especially those having high sp\(^3\) content known as ta-C. The sp\(^2\) hybrids provide the other extreme of such properties; providing highly conductive materials, exceptional optical properties and mechanical strength along one or two dimensions as those observed in carbon nanotubes and graphene, respectively. As illustrated in Figure 1.3, defective graphene at the sp\(^2\) side of the spectrum can include some sp\(^3\) content as a result of the synthesis conditions, such as the case of chemically derived graphene (CDG) and graphene deposited by chemical vapor deposition (CVD-G).

The third type of hybridization known as sp\(^1\), results when the S-orbital is mixed with one P-orbital forming a single σ-bond and two π-bonds. This exists, for instance, when carbon atom is bonded to hydrogen.

As a result of the wide range of physical properties exhibited by its allotropes, carbon is highly useful element both in nature and in every day technology. In addition to being one of the most sought after natural materials, thin films of diamond have been synthesized by chemical vapor deposition
(CVD)\textsuperscript{6} to improve the mechanical and tribological properties of cutting tools and enhancing their wear resistance by being applied as a coating\textsuperscript{7}. CVD diamond is also used for thermal management in electrical circuits or high-power laser diodes\textsuperscript{8}, due to its very high thermal conductivity and electrical insulating properties as compared with other insulators\textsuperscript{9}.

Amorphous carbon thin films have also been widely used as wear and corrosion protection coatings with the advantage of being formed at lower processing temperature than CVD diamond. Diamond-like-carbon (DLC) is a type of amorphous carbon exhibiting a high fraction of sp\textsuperscript{3} hybridized atoms, hence it inherits most of the desired properties of crystalline diamond in terms of hardness and chemical inertness\textsuperscript{10}. DLC thin films have been used extensively as protective coating in several areas such as magnetic hard drives, micro-electromechanical systems and car parts. DLC films were also utilized as durable coatings for body implants because of the low surface friction, corrosion resistance and biocompatibility of such films\textsuperscript{11}.

The mechanical and electrical properties of carbon nanotubes (CNT) are quite extraordinary\textsuperscript{12}, they exhibit a carrier mobility of $\sim 10000 \text{ cm}^2/\text{Vs}$ with an electrical current density of $\sim 4 \times 10^9 \text{ A/cm}^2$. 

*Figure 1.3: Some applications of planar films of carbon allotropes based on the sp\textsuperscript{3} and sp\textsuperscript{2} contents.*
and elastic modulus of 1 TPa with a tensile strength of 100 GPa. CNT have been used in the form of powders in many applications such as a reinforcing material in polymers and ceramics and as a source of electrons emission in field emitters. Thin films of CNT have opened the doors to many other applications such as high efficiency nanoparticle filters, transparent flexible electrodes and electrochemical sensors. Practical magnet-free loud speakers were tailored from flexible and transparent CNT thin films, and they showed competing results in terms of frequency range response and sound pressure.

The most recently discovered carbon allotrope, graphene, has become a hot research topic resulting from its pure sp² hybridization, which is responsible for its extraordinary electrical, mechanical and thermal properties. Such films can be used as transparent conductive electrodes for a variety of applications, including displays and solar cells, as a chemical sensor with single molecule sensitivity, nanomechanical resonators and field emitters. Recently, IBM reported the first integrated circuit fabricated using graphene based field effect transistors (FETs). Demonstrated graphene based FETs has operating frequencies up to 300 gigahertz in a device with a channel length of 140 nm. In addition, Solution processed graphene oxide has been used to deposit large scale thin-films which can subsequently be reduced to form transparent conductive electrodes for solar cells applications, having sheet resistance of $10^2 - 10^3 \Omega/$square with 80% transmittance.

### 1.2 - Motivation

In the magnetic storage industry, an ultrathin DLC overcoat (<< 10 nm) with high sp³ content is required to provide corrosion protection, as well as protection against mechanical wear for both the magnetic layers and read/write heads. As one of the fastest growing industries, the magnetic storage industry requires higher storage density which is projected to exceed 1 Tbits/inch² in the future. The DLC coating on the surface of the magnetic disk and the read/write head forms a vital component in hard drives, being responsible for protecting such parts against corrosion and mechanical wear. Thickness of such coatings is a determining and limiting factor of the storage density, as larger
separation between the rotating disk and the reading head decreases the storage density\textsuperscript{26}. Achieving ultrathin DLC films of thicknesses around 2 nm would increase the storage density to 1 Tbits/in\textsuperscript{2}, however difficulties in deposition of continues sp\textsuperscript{3}-rich films at such small thickness with conventional techniques such as sputtering are not yet overcome, in large part due to the low ionization fraction and ion-to-neutral arrival ratio of sputtering. Filtered cathodic vacuum arc (FCVA) deposition has been recently proposed as an alternative method to depositing ultrathin, high sp\textsuperscript{3} content carbon films, due to the fact that the overwhelming majority of deposited species are ionized and participate in the ion bombardment, which imparts sufficient kinetic energy to the growing film to activate sp\textsuperscript{3} hybridization as well as continuous film formation \textit{via} a subplantation or shallow implantation process. As this is a technique currently under development, the deposition conditions are not well optimized yet. The first half of contributions in this thesis will therefore focus on structural properties of DLC films deposited by FCVA on model Si substrates.

Oxidation of graphene is becoming increasingly significant process in tuning the properties of pristine graphene as well as providing solution processed routes for large scale deposition of graphene thin films. Solution processed graphene oxide (GO) is becoming a main route for depositing thin films of graphene; however, the presence of oxide species on graphene sheets has inhibited the extraordinary properties of graphene. Hence, deposition is followed by a reduction process to remove the oxide species and restore the properties of pristine graphene. Residual defects and oxide species were always observed even after the reduction process, failing to restore the pristine properties of graphene. Pristine graphene exhibits a carrier mobility of \(\sim 10000\) cm\textsuperscript{2}/Vs \textsuperscript{27}, whereas, for a thermally reduced GO thin film it was reported to be 281 cm\textsuperscript{2}/Vs \textsuperscript{27}, which represents 3\% of that for the pristine sheet!

A better understanding of the oxidation process and associated structural variation could enable better techniques to reduce GO and restore most of the properties of pristine graphene, as well as more controlled tuning of its properties. The second contribution of this thesis will focus on
investigating the structural and chemical modifications of graphene sheets during low-pressure plasma oxidation.

Ultra-thin planar carbon layers at the two extremes of sp\(^3\) and sp\(^2\) hybridizations exhibiting highly sought after properties will therefore be the subject of this thesis’ investigation, as outlined below.

1.3 - Thesis outline

In the upcoming chapter (Chapter 2), we review the synthesis and properties of two carbon materials, namely the sp\(^3\) rich diamond-like carbon in the context of magnetic storage media, and the sp\(^2\) graphene and its gradual oxidation process, in the context of transparent conducting electrode applications. The chapter concludes with a review of spectroscopic analysis techniques of carbon materials, focusing on X-ray photoelectron spectroscopy and Raman spectroscopy, as well as related structural models. Chapter 3 is intended to be a reference for subsequent chapters, as it describes the various experimental methods used throughout this thesis. In Chapter 4, we present the structural investigation of ultrathin DLC films deposited by FCVA method on model Si substrates. In Chapter 5, we focus on graphene oxidation via low pressure plasma and investigation of its structure and composition. The final chapter (Chapter 6) summarizes the results and conclusions, discusses the thesis, and presents future perspectives.
Chapter II

Towards the extremes of hybridization: $sp^3$ and $sp^2$ planar carbon materials
Scientists and engineers have been trying to capture the extraordinary properties of carbon by investigating efficient routes and providing better understanding for obtaining planar materials, namely ultrathin films, at the extremes of bonding configurations shown in Figure 1.3, namely, the pure sp³ and pure sp² hybridized carbon. Moving towards higher sp³ contents enable the extraordinary hardness, tribological properties and low friction coefficient of carbon. Such properties are essential in a variety of applications requiring protective coatings. DLC films, which may be synthesized using a wide range of methods, represent the cheaper and more efficient replacement of CVD diamond in such applications, and have been used extensively as overcoats in hard drives as will be reviewed in section 2.1. On the other end of the spectrum, purely planar sp² carbon allotrope such as graphene enables extraordinary electrical properties while remaining highly transparent. Unfortunately, graphene remains difficult to synthesize. Graphene, in the form of reduced graphene oxide, has therefore been extensively explored as transparent electrode for solar cells and interactive displays. Graphene, its various synthesis routes and the structure of graphene oxide and its reduction methods are reviewed in section 2.2. A brief review of spectroscopic analysis methods used in this thesis and critical to structural and chemical analysis of carbon materials using Raman Spectroscopy and X-ray photoelectron spectroscopy follows in section 2.3.

2.1 – Diamond-like Carbon (DLC) films for magnetic storage devices

2.1.1 - Structure of magnetic storage devices

Computer hard drives utilize ultrathin carbon coatings on the surface of the magnetic disk and read/write heads as protective layer against corrosion and mechanical wear. Improvements in the properties of these overcoats and the ability to deposit ultra-thin layers with thicknesses less than 10 nm have lead to the development of hard drives with large storage density and small portable size, as we know them today.

In Figure 2.1, the two main components of a magnetic storage device are shown, namely the rotating disk on which the data is stored and the read/write head scanning the surface of the disk. The
rotating disk consists of a thin film layer of Co-Cr-Pt alloy, deposited on a alumina or glass substrate pre-coated with Cr-based texture layer and a Ni-P base layer. The magnetic layer is subsequently coated with a thin protective carbon coating designed to prevent corrosion and wear of the active layers. A molecular lubricating layer of a perfluoro-polyether, such as ZDOL, is deposited as the top layer to reduce the friction coefficient of the assembly at the head-disk interface. A slider arm holds the read/write head made of (Al₂O₃-TiC) above the rotating disk; it is also protected with a similar carbon coating.

Figure 2.1: Main components comprising a magnetic hard drive, including a rotating disk and a read-write head. Typical coating structure including the carbon overcoat is also illustrated.

Current generation hard drives consist of several rotating disk and read/write head assemblies stacked on top of each other. The read/write heads slide over each disk attached to a comb-like sliding arm. The overall capacity of a hard drive is determined by the total number of rotating disks and the capacity of each. As the storage capacity of hard drives increases, the requirement to hold increasing numbers of disk/head assemblies is not easily scalable. Larger number of disk/head assemblies increases the probability of mechanical crashes resulting in loss of data, while the speed of rotation and reading/writing process is limited by the large diameter of individual disks. Moreover, the storage density has been increasing at an annual rate of 100% as shown in Figure 2.2, which can only be sustained by further developments of the storage density. For these reasons, the storage
density on the rotating disk is a significant factor that must be continuously improved for the development of faster and more compact hard drives.

![Figure 2.2: Growth of storage density over the past two decades. Lab demonstrations are represented in large solid dots, whereas actual commercial products are represented by small dots](image)

### 2.1.2 – Factors affecting the storage density

In magnetic storage devices, data is stored along concentric tracks on the surface of the rotating disks, wherein a single unit of data is known as the bit. Storage density, defined as the number of tracks per inch multiplied by the number of bits per inch along the track, have been doubling every year since the discovery of the first hard drive by IBM known as RAMAC in 1956. At that time, RAMAC boasted a storage density of 2 Kbits/inch². Enhancement of storage density has been facilitated with continuous improvements in the read/write head, magnetic layer and the interface between the two mentioned parts. In general, the storage density of a magnetic layer is limited by thermal stability of the materials in terms of the super-paramagnetic limit, at which the thermal energy can overcome the coercive energy of the magnetic bits resulting in loss of the stored data, this limit was around 40 Gbits/inch² in 1995. The introduction of perpendicular recording technology has increased this limit to 1000 Gbits/inch², as the bits are stored in orthogonal direction to the rotating disk, in contrast to the conventional longitudinally recorded bits. Currently, Toshiba holds
the record for the highest storage density hard drives, which has achieved 541.4Gbits/inch² using the perpendicular recording technology. Attempts to approach the limit of 1000 Gbits/inch² have focused on reducing the area occupied by a single storage bit. The spacing between the read/write head and the magnetic storage layer, also known as the magnetic spacing, limits the minimum size of a bit critically. Smaller spacing leads to smaller area occupied by a single bit, leading to larger storage densities, as shown in Figure 2.3. To reach the 1000 Gbits/inch² limit, the magnetic spacing has to be reduced down to 6.5 nm, thereby fixing the thickness of the protective carbon overcoat to ~ 1-2 nm. This is a major challenge, since conventional thin film deposition techniques, such as sputtering, fail to produce a continuous carbon coating at thicknesses below ~ 5-6 nm.

![Figure 2.3](image)

Figure 2.3: Variation of storage density with the spacing between the magnetic layer and read/write head (also known as the magnetic spacing). Also shown are the effects of the fly height, disk carbon thickness and slider carbon thickness.

2.1.3 - Requirements of carbon overcoats

The main requirements of the ideal carbon protective overcoat are to provide protection to the magnetic layer from corrosion and mechanical wear and to be compatible with the other components of the disk and the overall function of the hard drive as shown in Figure 2.4. Forming a continuous, dense film coating for the magnetic layer is vital to providing protection against corrosion, and
prohibiting the permeation of any reactive chemicals to the magnetic layer. Mechanical and wear protection are also needed to prevent scratches during head crashes, requiring overcoats to exhibit high hardness, high elastic modulus and low friction coefficients.

The overcoat should also provide a good support to the lubricant at the head-disk interface, providing ideal separation from the magnetic layer and the metallic components in the head to avoid degradation of the lubricant. For that reason, the carbon overcoat should be compatible with the lubricating layer and provide it with a smooth, stable and pin-hole-free supporting surface for the perfluoro-polyether lubricant to spread and move on. The requirement for smooth surface is doubly important as the overcoat should not interfere with the movement of the read/write head above the magnetic disk.

![Figure 2.4: Key requirements of DLC overcoats and their corresponding properties.](image)

### 2.1.4 - Types of DLC

Physical properties of carbon overcoats are strongly related to the structure of the film, which in turn varies with the deposition technique used and the corresponding growth conditions. Diamond-like carbon films are amorphous carbon (a-C) with significant portion of sp³ bonding, which can vary from 20% up to 90% as in tetrahedral amorphous carbon (ta-C), and can exist in a hydrogenated form (ta-C:H) with a possible hydrogen content up to 60%. Traditionally, a-C films were used for magnetic hard drive protection, which was then replaced by a-C:H as the hydrogen incorporation
was proven to improve the tribological properties of the lubricant/carbon interface both in terms of adhesion and wear protection\textsuperscript{28, 34}. A drawback of hydrogenated films is that the lubricant can degrade when stressed, emitting fluorine, which then reacts with the hydrogen to form HF and threatens to corrode the magnetic layers\textsuperscript{26}. Prevention of this issue while maintaining the benefits of hydrogenated films was achieved by nitrogen incorporation; nitrogenated amorphous carbon (a-C:N) showed improved tribological properties and toughness\textsuperscript{26}; however, it ceases to provide continuous surface coverage in the ultrathin thickness regime, due to limitations in growth behavior, as will be discussed in the next section. Most recently, the higher sp\textsuperscript{3} content films ta-C have exhibited the most desired properties, providing continuous, smooth films at thicknesses as low as 2 nm, while also exhibiting superior mechanical properties\textsuperscript{35, 36, 26, 37}.

\textbf{2.1.5 - Deposition methods}

In general, formation of a continuous and smooth DLC film requires large nucleation density of carbon islands on the surface, combined with low surface diffusion of the adatoms in order to prevent Ostwald ripening and island growth. This requirement restricts the deposition processes to ones where the impinging flux contains a large fraction of energetic species as compared to neutral ones, i.e., a high ion-to-neutral flux ratio, wherein the kinetic energy of most incident species exceeds the nucleation energy barrier, thus causing significant island breakup, while also causing significant subplantation via shallow implantation of hyperthermal ions below the growth surface. The latter also prevents deposited species from migrating and segregating at the growth surface and assures continuous mixing of deposited atoms and provides more homogeneous surface coverage\textsuperscript{28}. The mean kinetic energy of the impinging ions at the surface of the substrate plays a major role in determining the properties of DLC films. The sp\textsuperscript{3} content, the buildup of compressive stresses and the corrosion resistivity have all been correlated with ion bombardment energy\textsuperscript{36}. Ion bombardment during thin film deposition increases the amount of energy deposited per carbon atom, thus resulting in increased sp\textsuperscript{3} content even in low temperature processes\textsuperscript{10}. While relatively high ion energy (~ 100
eV)\(^{10}\) is needed to form sp\(^3\) hybridized carbon in thin films, excess ion energy can also modify the underlying substrate and reduce the growth rate of the film due to resputtering of carbon atoms\(^ {38}\).

Carbon films have been deposited using several techniques, each with its own advantages and shortcomings. Among these, sputtering is currently favored due to its simplicity, efficiency, and low cost\(^ {33}\). Sputtering has been used extensively to deposit a-C, whereas reactive sputtering is used to deposit a-C:H and a-C:N films. Typically, the sputtering process includes three main components, including a metallic or non-metallic solid-state target material, non-reactive and/or reactive process gases, and the substrate upon which the atoms sputtered from the target are deposited, as illustrated in Figure 2.5. Conventionally, Argon plasma is used to sputter a graphitic electrode, thus ejecting carbon species that condense on the substrate. The latter can be further biased to accelerate the ionized species (carbon and Ar) into bombarding the growing DLC film. A magnetron sputtering source is commonly used to increase the sputtering rate by enhancing the ionization density near the surface of the target, resulting in enhanced process efficiency and increased deposition rate.

![Schematic representation of a sputter deposition process.](image)

Ion beam sputtering can also be used to enhance the sputtering rate of the target. Here, the process gas plasma is replaced with an Ar\(^+\) ion beam source to sputter the target, while a second ion beam can be used to bombard the growing film on substrate in what is known as dual ion beam
deposition. Ion beam deposition techniques, wherein carbon ions — generated by sputtering of a graphitic sample or ionization of a hydrocarbon gas are extracted through a biased grid and accelerated towards the substrate (see Figure 2.6) have also been used to form DLC films.

![Figure 2.6: Schematic representation of an ion beam deposition process.](image)

The main drawback of sputtering techniques is the very low fraction of ionization of the process gases and the resulting low average energy deposited by incident atom. This leads to a smaller sp³ content and formation of non-continuous films for thicknesses below 5-6 nm.

Among the most interesting techniques used widely in laboratory studies is plasma enhanced chemical vapor deposition (PECVD; see Figure 2.7). This technique utilizes vaporized hydrocarbons as the source of carbon, and strikes a plasma using RF excitation between two electrodes, thus ionizing and fractionating the reactant species. A self-bias develops between the plasma and the electrodes due to the difference in mobility of heavy ions and much lighter electrons. By designing the cathode to be much smaller than the anode, typically by utilizing a grounded metallic chamber as the anode, a much larger negative self-bias develops on the cathode, where the substrate is typically placed. The positive carbon ion species therefore accelerate through the sheath toward the substrate holder and bombard the surface of the growing DLC film. The main advantage of this technique is that the plasma is free of macroparticles often ejected during erosion of solid-state sources used in sputtering processes; hence, a more continuous film can be obtained. PECVD suffers from lower deposition rate and sp³ fraction due to the small fraction of ions in the chamber and the fact that operating conditions are not global since deposition conditions depend upon system geometry.
Recently, filtered cathodic vacuum arc (FCVA) has been proposed as one of the most promising techniques for depositing ta-C films, due to very high ionization fraction of deposition species. FCVA shares the same working principle as arc deposition techniques illustrated in Figure 2.8. A high current arc discharge is generated between two electrodes: a cathode source material and anode substrate. A high temperature arc vaporizes the cathode material into high density plasma containing carbon ions, neutral carbon and macroparticles. The carbon plasma is then directed towards the substrate where a thin films forms.

The added feature in FCVA is the use of a magnetic filter which removes non-ionized species and macroparticles to increase the purity and ionization of the plasma and obtain low-defect films with high sp\(^3\) fraction even at elevated deposition rate. The magnetic field directs the ionized species of
the plasma to flow into a curved duct as shown in Figure 2.9. Both electrons and ions follow its lines along the curved path, preserving the neutrality of the plasma, and reach the substrate. As neutral species and macroparticles are not affected by the magnetic field, they are trapped by the walls of the curved duct. After passing the filter, the highly ionized carbon plasma interacts with the substrate resulting in thin film deposition. The substrate is typically biased to increase the kinetic energy of the ions and to enhance and control the properties of the films.

Filters consisting of ducts having more than a single curve or bend have been developed to increase macroparticles filtering efficiency (see Figure 2.10). As such, S-bend filters have proven to be more efficient than single-bend filters at removing macroparticles scattered off the walls of the chamber and at increasing the ionization fraction of the plasma.

Plasma fluctuation in FCVA is one of the main drawbacks of arc techniques. Such fluctuations result from instabilities in the arc current and can lead to process reproducibility issues, as well as non-uniform cathode erosion. Such problems have been circumvented by the use of a pulsed mode arc discharge, wherein constant regeneration of the arc during deposition helps to evenly move the arcing spot on the cathode. On the downside, pulsing reduces the deposition rate as compared with the conventional dc arcing mode.

Figure 2.9: Schematic representation of magnetic filters used in FCVA deposition.
Magnetic steering of the arcing spot in the dc arcing mode using a magnetic filter at the cathode was demonstrated by Zhang and Komovopoulos\textsuperscript{38} to address the main concerns of non-uniform target erosion of the conventional dc arcing mode and the low deposition rate of pulsed arcing mode. The highly ionized plasma, narrow and tunable energy distribution and the high deposition rate make FCVA a very compelling process for deposition of the protective carbon overlayer for magnetic storage media.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_10.png}
\caption{Magnetic filters used to remove macroparticles from FCVA plasma\textsuperscript{26}. a) Single-bend filter, b) S-bend filter}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_11.png}
\caption{The RMS surface roughness as a function of the thickness for FCVA-deposited DLC films. The apparent roughness increase of the thinnest FCVA films was attributed to the rougher silicon substrate. From reference \textsuperscript{41}.}
\end{figure}

Previous work on FCVA deposited DLC has shown that the sp\textsuperscript{3} content of films is lower in ultrathin films than for thicker films\textsuperscript{41}. Thin films with \( \sim 70 \) nm thickness deposited without substrate biasing exhibited \( \sim 88\% \) sp\textsuperscript{3} content and an elastic modulus of \( \sim 750 \) GPa, whereas ultrathin films of \( \sim 4 \) nm deposited under identical conditions exhibited only \( \sim 50\% \) sp\textsuperscript{3} content and an elastic constant of
100 GPa. Surface roughness was also correlated to film thickness, showing a slight decrease of root mean squared (RMS) roughness with increasing film thickness as shown in Figure 2.11.

In the absence of substrate biasing, the intrinsic ion energy of carbon atoms in the plasma of a cathodic arc deposition system is calculated to be \(~19\) eV \(^{42}\). This energy falls short of what is required to provide high \(sp^3\) content. Amorphous carbon films were observed to approach the desired DLC properties at an energy of \(~120\) eV \(^{35,37,43}\). Hence substrate biasing is a must for synthesizing DLC films using FCVA.

Zhang and Komvopoulos\(^43\) have further investigated the influence of deposition time (film thickness) and substrate bias and have reported films with an \(sp^3\) content of \(~45\)% when utilizing substrate bias conditions of \(-150\) V. Further increase of the substrate bias resulted in reduced \(sp^3\) content as shown in Figure 2.12a. This is believed to be due to ion bombardment-induced relaxation of stresses, atomic diffusion and decreased \(sp^3\) content\(^43\). A correlation was also observed between deposition time and \(sp^3\) content for durations less than 30 s and substrate bias of \(-100\) V. Smaller deposition time also led to lower \(sp^3\) content as shown in figure 2.12b.

![Figure 2.12: Carbon constituents of the deconvoluted C1s core level peak with respect to (a) substrate bias and an ion fluence of \(3.6 \times 10^{16}\) ions/cm\(^2\) and (b) to processing time (and ion fluence) for fixed substrate bias of \(-100\) V. Both experiments are performed using pulsed DC arc mode at a frequency of \(25\) kHz.\(^43\).](image)

This was explained in terms of the subplantation model of \(sp^3\) carbon formation, according to which \(sp^3\) hybridization is controlled by subsurface mechanisms, whereby densification of the deposited carbon \(via\) subplantation of incoming carbon ions lead to formation of higher \(sp^3\) content in the
depth of the film. However, this requires that approximately 1.5 nm of carbon be deposited for the impinging ions to cause substantial structural changes.

2.2 - Graphene and its structural modification via plasma oxidation

2.2.1 - History and discovery of graphene

Graphene is a two dimensional crystal consisting of a continuous layer of sp² hybridized carbon connected in a honeycomb network. It can be thought of as the building block for other carbon allotropes. A 2D graphene layer can be wrapped to form a 0D fullerene or rolled into 1D carbon nanotube, or stacked to form 3D graphite as shown in Figure 2.13.

The properties of graphene as a single layer of graphite have been studied extensively – theoretically and computationally – during the past century. However, the physical existence of such a single atomic layer was considered to be not possible. The idea of having free standing 2D crystals in general was rejected as several studies concluded that the melting temperature of thin films is directly proportional to thickness. As a result, single-layer materials were considered to be unstable, tending to segregate into three dimensional clusters of material.

However, in 2004, a single layer of graphene was isolated for the first time by peeling off atomically thick layers from graphite using adhesive tape, this simple achievement changed the way the research community thinks of two dimensional crystallites, and opened the door for studying the
properties of such materials experimentally. The strong sp² bonds in the plane of the monolayer are believed to have stabilized the 2D crystal against thermal effects. This discovery has since then put graphene under the spotlight and made it one of the most exciting materials of our times.

The properties of graphene depend very much upon the thickness, or number of layers. The extraordinary properties of graphene are observed only up to a certain number of layers, above which it mimics the behavior of bulk graphite. A classification of graphene based on the number of layers, and hence the properties has also been established. It divides graphene thin films into a single layer graphene with one atomic thick two dimensional structure, bilayer graphene with two layers of carbon stacked in A-B bernal configuration. When the number of layers exceeds 3 atomic layers, it is considered as a graphene ultrathin film up to 10 layers, after which the properties of three dimensional graphite are observed, as also confirmed by electronic structure calculations.

2.2.2 - Applications of graphene

In spite of its very recent discovery, much effort has being expended to exploiting graphene in a wide range of applications, owing to its extraordinary electrical, optical, thermal and mechanical properties. It is being explored by the semiconductor industry as a potential replacement for silicon in field effect transistors and electronic integrated circuits owing to its superior carrier mobility. The fundamental limit for mobility in graphene is predicted to be 200000 cm²/Vs at room temperature, however for actual samples this value reduces to around 15000 cm²/Vs due to defects and substrate effects. Even with its reduced properties, graphene remains superior to other materials, including by its weak dependence on temperature and doping, which makes it an attractive material.

The use of graphene as chemical and biochemical sensing material is also attracting attention as a result of the low resistivity of graphene (1 µΩ.cm) compared to silver, whilst having the added advantage of the highest specific surface area of any material. Graphene-based sensors exhibiting single-molecule sensitivity were recently demonstrated, taking advantage of the high signal-to-noise ratio, ambipolarity, and sensitivity of its band structure to the presence of adsorbed species.
Graphene as transparent conducting electrode for photovoltaic and interactive displays applications have also gained special attention owing to the very high electrical conductivity, optical transparency, and the potential for large area deposition methods. Reduced graphene oxide films were recently reported with conductivities in the range of ~ 1000 S/cm and a transmittance of 80%\(^2\). CVD role-to-role production of graphene have been demonstrated, and were incorporated in fully touch screen devices exhibiting 97.4% transparency and sheet resistance of ~ 125 $\Omega$/square\(^5\).

The mechanical properties of graphene were investigated, revealing a Young’s modulus of 1 TPa and a strength of 130 GPa\(^5\). This has opened up new possibilities for graphene in nanomechanical devices and composites. Radio frequency resonators were demonstrated by using reduced graphene oxide ultrathin films exhibiting a quality factor of ~ 4000 which is comparably better than diamond resonators exhibiting values of ~ 3000\(^2\). The use graphene in composites has also attracted attention, as it has been used to make thermally and electrically conductive plastics (thermal conductivity of graphene is 3000 W/mK)\(^5\). Such applications will rely heavily on the availability of large-scale production methods of graphene powders that can be uniformly dispersed into a polymer matrix.

### 2.2.3 - Synthesis of Graphene

Fabricating single-atom-thick layers of graphene is still a challenging task. Research focusing on finding high yield methods or optimizing existing ones for getting large scale monolayer graphene is very intense. Ideally, the synthesis technique should be able to provide high quality crystals with control over the number of layers and with feasible large area production.

The first successful monolayers of graphene were obtained by micromechanical cleavage of graphite; either by drawing the crystal on a solid surface resulting in various single and multilayer graphene sheets\(^1\) or by using an adhesive tape to repeatedly peel flakes from the surface of highly oriented pyrolytic graphite (HOPG)\(^5\). Such methods are able to provide high quality monolayer graphene with
lateral sizes of up to 100 µm\textsuperscript{5,18} exhibiting high mobility of around 10000 cm\textsuperscript{2}/Vs. Such flakes are suitable for research purposes to test fundamental properties. However, the associated low throughput is a limiting factor for mass production, because single flakes are hidden between the thicker ones and are often difficult to characterize and observe\textsuperscript{17-18}.

Compromising on the quality requirement of graphene offers alternative means of fabricating large area graphene sheets exhibiting some of the exceptional properties of pristine films. Utilizing this strategy, multilayered, distorted and defective graphene films can now be produced by several techniques with sufficiently good electrical and mechanical properties. Such films are possible candidates for use in many of the potential applications mentioned above.

Current graphene fabrication methods can be generally classified into substrate-based methods, and non-substrate-based methods. Substrate-based methods are those in which the growth of graphene is restricted to certain types of materials that catalyze and support the process, including both epitaxial graphene on SiC\textsuperscript{52} and chemical vapor deposition (CVD) graphene from a hydrocarbon vapor on a transition metal surface\textsuperscript{53}. Annealing of a SiC substrate at ~ 1500 °C results in formation of graphitized islands of carbon on the top of the substrate, as the Si desorbs from the surface at around 1000 °C. This process has been demonstrated to hold in ultra-high vacuum or ambient pressure conditions\textsuperscript{54}; monolayer wafer sized graphene with smoother morphology and larger crystalline domains were achieved in vacuum conditions, with a carrier mobility of 2000 cm\textsuperscript{2}/Vs \textsuperscript{52}.

Chemical vapor deposition (CVD) of graphene from a hydrocarbon vapor on a transition metal surface is extensively used for fabricating large scale graphene sheets\textsuperscript{53,55,56}. Typically, CVD processes are comprised of five main steps (see Figure 2.14), including delivery of the source gas into a chamber, followed by decomposition of the gas into reactive species, which are subsequently transported to the substrate allowing nucleation and film formation, and finally desorption of by–products of the reaction\textsuperscript{57}. 

CVD growth of graphene is a three step process\textsuperscript{54}; starting with loading the metal foil (Cu or Ni) into the furnace and filling with hydrogen while heating up to around 1000 °C, then the hydrocarbon gas such as methane (source of carbon species) is introduced into the reaction chamber at specified pressure and duration. The reactant decomposes thermally into reactive species, until finally cooling of the furnace down to room temperature induces nucleation and growth of graphene on the surface of the transition metal foil.

![Figure 2.14: Schematic representation of CVD film deposition process.](image)

CVD of graphene can be applied in both atmospheric pressure CVD (APCVD)\textsuperscript{56} and low pressure CVD (LPCVD)\textsuperscript{55} settings. LPCVD is commonly processed in the range of 1-10 mTorr compared to 760 Torr in APCVD\textsuperscript{58}. Reactors of thermal CVD can be hot wall, whereby the walls of the chamber are heated, or cold wall reactors. Hot wall reactors have the advantage of providing more uniform distribution of temperature leading to a more uniform film growth and higher growth rates.

Large-area single- to few-layers graphene films have been successfully obtained by CVD, achieving carrier mobility of around 4000 cm\textsuperscript{2}/Vs in case of the low pressure CVD process\textsuperscript{55}. The quality of graphene films depends strongly upon the choice of the transition metal substrate. For instance, using Cu foils increases the uniformity of the film and can result in monolayer graphene due to the low solubility of carbon in copper. On the other hand, Ni results in non-uniform graphene film formation with thicknesses that range from monolayer to tens of layers\textsuperscript{56}, likely due to the higher...
solubility of carbon in nickel and the associated difficulties to control the carbon precipitation at the surface during the cooling stage.

For substrate-based methods to be practical and economical, techniques for transferring graphene to other substrates, typically insulators or semiconductors, without damaging the graphene layer are necessary. Such a technique has been suggested for transferring CVD graphene from the Cu foil substrate. It consists in depositing PMMA on top of the sample, followed by etching of the metal substrate leading to a PMMA-graphene sample which can subsequently be placed on any desired substrate, followed by dissolution of the PMMA layer in acetone. Equivalent methods for graphene removal from SiC have not yet been reported.

Solution processing of graphene either in its pristine form or in a chemically modified structure may provide large scale, easy to process and low-cost routes for getting wafer scale thin films that can be integrated onto any substrate or device, making it potentially one of the most attractive routes. Within this category, the chemically derived graphene (CDG) is the best established process. Graphite is exfoliated by chemical methods leading to functionalized graphene sheets having a modified structure but exhibiting only some of the features of pristine graphene. The most popular CDG for thin film deposition is graphene oxide, which is synthesized by oxidation of bulk graphite in the presence of a strong acid. Oxygen groups are incorporated into every single sheet in the bulk structure of graphite, leading to formation of hydrophilic graphene oxide sheets. Water molecules easily intercalate and facilitate the exfoliation process and may be aided by a mechanical stimulant such as ultrasonication. The resulting graphene oxide sheets can form a homogenous dispersion in aqueous solution and other polar solvents, because the negative surface charge from oxide species leads to electrostatic stabilization. Aqueous solutions are therefore able to sustain a concentration of GO of ~ 3 mg/mL. Flake sizes vary widely from few nanometers up to several micrometers depending on the oxidation procedure and mechanical sonication during the exfoliation process. Excessive ultrasonication has been shown to break the flakes into smaller pieces. The most common...
oxidation process is Hummer’s method, which uses less hazardous chemicals when compared to other methods and yields high solution concentrations and flake sizes up to 30µm. Large area solution processing of CDGs, including GO, is subsequently achieved by a variety of techniques, including dip-coating, spin coating, spray coating, Langmuir-Blodgett self assembly and vacuum filtration. Models of GO have described the sheets as a defective sp²-carbon network incorporating various functional groups of oxygen at the interior and on the edges. A structural model presented by Lerf et al. is shown in Figure 2.15, showing epoxide (C-O), C=O and C-OH groups forming in the basal plane. Carbons at the edges are either terminated with C-OH or –COOH according to the model. Tetrahedrally bonded sp³ carbon also exist, shifting above and below the sheet. Accordingly, the benefits of easier processing of solution processed GO are confronted with the reality of dramatically reduced electrical conductivity of pristine graphene.

Figure 2.15: Structural model of GO. The position of oxygen functional groups is indicated by circles.

To recover the properties of pristine graphene, the oxide groups should be removed through a reduction process. Reduction of graphene oxide can be achieved by chemical methods through exposure to reduction agents, such as Hydrazine, by thermal annealing at temperatures up to 1100 °C or by a combination of both. Such processes can be applied either to the aqueous solution containing the sheets, dried GO powder or to the film after deposition, where the former is more efficient since both sides of the sheet are exposed to the reducing agent. Treatment in hydrazine has been
shown to be effective at removing only epoxy and hydroxyl groups from the basal plane of the sheet, leaving the carboxylic groups at the edges\(^67\). Becerril et al. tried the above mentioned reduction methods on deposited graphene oxide films; thermal annealing at 1100 °C showed the best results in terms of sheet resistance \((10^2-10^3 \, \Omega/\text{square})\) (see Figure 2.16) as compared with hydrazine treatment and combined treatment of hydrazine and thermal annealing at 400°C. Chowalla et al. reported large area films of reduced GO with sheet resistance of 600 \(\Omega/\text{square}\) and mobility values in the range of 10 to 15 cm\(^2\)/Vs, using a variety of reduction methods\(^62\). Clearly, the reduction process does not restore the properties of pristine graphene, as significant defects remain in the graphene film, carbon is lost through the oxidation process, and some amount of oxygen remains incorporated in the reduced graphene. Therefore, the development of successful reduction processes may benefit from improved understanding of the oxidation process, as seen in Chapter 5 of this thesis.

![Figure 2.16: Comparison of the sheet resistance of GO films with different optical transparency after undergoing reduction treatments indicated in the legend.](image)

2.2.4 - Tuning the properties of Graphene via confinement and functionalization

Chemical and structural modifications of sp\(^2\) hybridized sheets of graphene can expand the range of applications in which graphene can be utilized. Physical modification of graphene by cutting it into
ribons\textsuperscript{68} and quantum dots\textsuperscript{69} have been used to modify its electronic structure, as the band gap increases from zero, in the semi-metallic state of pristine 2D sheets of graphene, to make it a semiconductor with tunable band gap. Confinement of electrons in two or three dimensions results in increased band gap. Semiconducting graphene was successfully obtained in the form of chemically derived nano-ribbons with widths below 10 nm\textsuperscript{70}. Another promising route is the functionalization of the surface of 2D graphene sheets with various reactive species through physicochemical treatment. Hydrogenation of graphene has been used to transform the conducting graphene into a semiconductor and an insulator\textsuperscript{71} depending on the surface coverage of hydrogen and associated loss of conjugation\textsuperscript{72}. Electron mobility was observed to be inversely proportional to the degree of hydrogenation\textsuperscript{73} as a result of distorting the sp\textsuperscript{2} network and forming sp\textsuperscript{3} (C-H) bonds. Fluorine has also been used to alter the properties of graphene by reducing the surface energy and increasing its hydrophobicity\textsuperscript{74}. Oxygen treatment of graphene has been most commonly investigated\textsuperscript{74,75,76}; luminescence can be observed after oxygen plasma treatment of mechanically exfoliated graphene\textsuperscript{75}, as well as formation of a band gap which enables its use in logic and switching devices\textsuperscript{76}.

Oxygen plasma treatment of graphene has been associated with structural modifications of the graphene crystal. Raman spectroscopy reveals defect formation in the plane of the sheets with prolonged oxidation\textsuperscript{76}. These defects can be classified in two types: a break in symmetry due to formation of sp\textsuperscript{3} bonds between carbon and oxide species\textsuperscript{74} and amorphization of the sp\textsuperscript{2} carbon through ion bombardment by energetic species in the plasma. Different forms of carbon-oxygen species were observed\textsuperscript{74}, epoxide or hydroxide(C-O), carbonyl (C=O) and carboxylic groups (-COOH), with the latter forming at the edges of the sheet while the first two decorate predominantly its surface\textsuperscript{69}. Hydroxide groups (C-OH) can also exist at the edges of the sheet.

Oxidation of graphene was also performed using thermal heating in an O\textsubscript{2}/Ar environment\textsuperscript{77}, revealing that the degree of oxidation depended upon the number of layers in graphene, revealing faster oxidation for single layers compared to double and triple layered graphene.
2.3 – Spectroscopic analysis of carbon materials

Spectroscopic methods are crucial for the structural and compositional analysis of carbon nanomaterials. Among these, X-ray photoelectron spectroscopy and Raman scattering stand out as two methods that are particularly well suited to investigate both DLC and graphene coatings, and are reviewed below.

2.3.1 - X-ray photoelectron spectroscopy (XPS)

XPS is considered as one of the most powerful tools available in surface science. It relies on the detection of characteristic photoelectrons emitted from the sample’s surface upon exposure to X-rays to identify elements and their bonding characteristics and local environment. When X-rays are absorbed by a sample, their energy is transferred into three main components (see Figure 2.17), including (1) breaking the bond between electrons and the atom, also known as the binding energy, (2) to provide sufficient kinetic energy to the photoelectrons located nearest to the surface to escape from the surface of the sample, and (3) to provide excess kinetic energy to the ejected photoelectrons in vacuum. The characteristic parameter among these energies is the binding energy, which allows to fingerprint elements and their binding environment 57.

![Figure 2.17: Schematic representation of the photoelectron effect.](image)

2.3.1.1 - XPS data analysis for C 1s peak

Typical XPS spectra are obtained by scanning the binding energy and measuring the associated intensity of photoelectron signal. Each peak in the spectrum can thus be identified and labeled with
the associated element and the shell from which the electron is emitted, as shown in Figure 2.18 in the case of a survey spectrum for oxidized CVD graphene on copper. A higher resolution scan of the C1s photoelectrons, i.e., of electrons ejected from the 1s shell of carbon, is shown in Figure 2.19 in the case of FCVA deposited DLC films.

![Figure 2.18: XPS survey spectrum for CVD graphene deposited on copper and exposed to oxygen plasma for 1 s seconds.](image-url)

![Figure 2.19: High-resolution XPS spectrum of the C 1s peak of CVD graphene exposed to oxygen plasma for 1 s seconds.](image-url)

The characteristic peak of carbon C 1s appears in the range of 283 eV to 290 eV, and it can be decomposed into several components depending on the structure of carbon and other existing
elements. Fitted peaks within the C 1s can either related to C-C bonds or to bonds of carbon with other elements. C-C bonds are revealed by three peaks\textsuperscript{78}; a peak from sp\textsuperscript{2} hybridized atoms appearing at 284.25 ± 0.30 eV known as C 1s-2 and another representing the sp\textsuperscript{3} hybridized atoms appears at 285.33 ± 0.38 eV known as C 1s-3, beside an sp\textsuperscript{1} peak that appears at 283 eV. Peaks from carbon oxygen bonding can appear at higher binding energies than the previous peaks, each referring to a different state of bonding. These peaks were identified as C 1s-4 for (C-O) appearing around 285.5 eV, C 1s-5 for (C=O) appearing around 287.7 eV and C 1s-6 for carboxylic (O=C-O) group appearing around 290 eV, respectively\textsuperscript{79}. For DLC, these peaks are referred to as satellite peaks as they aren’t used in analyzing the samples. The C 1s-3 peak can also refer to C-H bonding as observed in hydrogenated graphene samples\textsuperscript{72}; which was reported to appear at the same position as sp\textsuperscript{3} connected carbon atoms (C-C). (C-O) peak in XPS can refer to either epoxy or hydroxyl groups decorating the basal plane, while (C=O) indicates ketons and quinines at the edges of the sheet or carbonyl groups in the basal plane\textsuperscript{80}.

The relative content of each type of bonding within the C 1s can be found by measuring the area fraction of the peak representing that bond relative to the total area of the C 1s peak. This provides a direct and simple method of measuring the sp\textsuperscript{3} to sp\textsuperscript{2} ratio in amorphous carbon thin films, as well as the degree of oxidation and structural variations in CVD graphene making XPS vital component for analysis in this project.

**2.3.2 - Raman Spectroscopy:**

Raman spectroscopy (RS) is probably the single most commonly used method used to fingerprint carbon allotropes. RS is based on the interaction between photons and molecules, whereby a sample is irradiated with a monochromatic laser beam that excites molecules, causing them to vibrate and irradiate a photon with a different energy, based on photon-phonon interactions. Upon excitation of the atoms to a higher level, they either return back to their original state in what is known as Rayleigh scattering (elastic), or to a different energy level with either higher (Stokes) or lower (Anti-stokes)
energy than the initial state. The latter two processes are inelastic and are known as Raman scattering (see Figure 2.20). The energy and associated wavenumber shift of the irradiated photons depends on the phonon dispersion relations, which depend upon the intrinsic properties of each type of material, including the elements, bonding chemistry, long range order, and microstructure. The measured energy shift is therefore a characteristic fingerprint of the sample itself. Typical Raman spectra consists of energy shifts plotted against the detected intensity as shown in figure 2.22a for a typical DLC film spectrum and 2.22b for CVD graphene sample.

![Figure 2.20: Elastic (Rayleigh) and inelastic scattering (Raman) of photons upon excitation.](image)

### 2.3.2.1 - Main features of Raman spectra of carbon materials

Raman spectroscopy has been used extensively to study the entire order-disorder range of carbon materials, making identification of the main spectral features possible. The two main peaks that define a carbon spectrum are the so-called G-peak and the D-peak. The G-peak, which exhibits a single peak only appearing at 1570 cm\(^{-1}\), results from in-plane stretching of the sp\(^2\) bonded carbon (see Figure 2.22a) and appears in all carbon structures except in pure diamond, because the latter has no sp\(^2\) hybridized carbon. The spectrum of single crystal graphite consists only of a single sharp G-peak appearing at 1570 cm\(^{-1}\). The position of this peak is sensitive to the structure of graphene changes according to the level of disorder and can vary between 1565 cm\(^{-1}\) and 1600 cm\(^{-1}\). The D-peak centered at 1355 cm\(^{-1}\) is caused by the breathing mode of aromatic carbon atoms (see Figure...
2.22b), which is forbidden in pure graphite and becomes active only when defects or discontinuities in the symmetry of the network exist. Other first order Raman peaks appear in the range from 1000 cm\(^{-1}\) to 1800 cm\(^{-1}\); The D’-peak at \(\sim 1620\) cm\(^{-1}\) appears in relatively well ordered carbon materials, and its intensity is correlated with the degree of disorder in the sample similar to the D-peak\(^8\). The D''-peak at \(\sim 1500\) cm\(^{-1}\) is observed in carbon films, and appears at the valley between G-peak and D-peak when they emerge in disordered structures. Another minor peak – the I-peak - is reported at 1300 cm\(^{-1}\) \(^8\), and is related to the presence of impurity ions, hence its name.

\[
\text{Figure 2.21: Typical Raman spectra of carbon materials. (a) DLC film deposited by FCVA and (b) pristine CVD graphene on a copper foil.}
\]
Figure 2.22: Schematic representation of the vibration mode of carbon atoms, consisting of (a) the stretching mode causing the G-peak and (b) the breathing mode causing the D-peak.

In the second order range, extending from 2500 cm\(^{-1}\) to 3500 cm\(^{-1}\), peaks that are considered as overtones or combinations of the first order bands are observed in relatively ordered structures. A single broad peak at 2900 cm\(^{-1}\) is observed in more disordered structures, but splits into three peaks at 2700 cm\(^{-1}\), 2900 cm\(^{-1}\) and 3200 cm\(^{-1}\) with increasing order. The peak at 2700 cm\(^{-1}\) is known as the 2D peak, and it becomes more intense with increasing order, where the peak at 2900 cm\(^{-1}\) disappears. In graphite, the 2D peak splits into two components; a narrow peak at the higher wavenumber range and a broad peak at the lower wavenumber. The 2D peak is especially relevant to studies involving graphene.

The Raman spectrum of carbon materials is a function of sp\(^2\) clustering, bond disorder, presence of sp\(^2\) rings or chains and of the sp\(^3\)/sp\(^2\) ratio, and hence it has been used to investigate and characterize the structural ordering\(^{81,82}\), sp\(^3\) content in DLCs\(^{83,84}\) and more recently in detecting graphene and determining its thickness\(^{85}\).

Both G and D peaks have been used to detect disorder in the structure as well as the sp\(^3\) content in DLC by evaluating their spectral positions, widths and intensities. Disorder in carbon is defined as either bond distortions or hybridization of the sp\(^2\) bonds into sp\(^3\). The evolution of Raman spectra over the order-disorder range of carbon structures have been described by Cuesta et al.\(^{81}\) by studying 29 types of carbon structures covering the entire order-disorder range, and is summarized in Figure 2.23. The main observations are that the D-peak and D'-peak intensities are directly related to
disorder; the D-peak width is correlated to the degree of disorder over the entire order-disorder
transformation range; the G-peak width is only correlated for well ordered materials and should be
ignored as a universal disorder parameter.

<table>
<thead>
<tr>
<th>Least organized materials – low rank coals and pitch</th>
<th>Least ordered solids</th>
<th>Little more ordered</th>
<th>more order</th>
<th>Much more order</th>
<th>Most Ordered (Graphite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Wide and asymmetric band with a single maximum near 1600 cm⁻¹</td>
<td>• Spectrum structured into two bands: G (1550 cm⁻¹) and D (1350 cm⁻¹)</td>
<td>• G-peaks start to get narrower and move towards a lower wave number</td>
<td>• D-band becomes progressively narrower and 2nd order peak splits into three peaks @2700 cm⁻¹, 2600 cm⁻¹ and 3200 cm⁻¹</td>
<td>• D-peak and G-peak, have similar width, but D-peaks become progressively weaker</td>
<td>• D-peak disappears completely</td>
</tr>
<tr>
<td></td>
<td>• Both peaks are very wide and have similar intensities</td>
<td>• Small signal in the 2nd order spectra @ 2900 cm⁻¹</td>
<td></td>
<td></td>
<td>• The second order peak at 2700 cm⁻¹ gains intensity and splits into two peaks; including a narrow peak with higher wave number and a broad one a lower wave number</td>
</tr>
</tbody>
</table>

Figure 2.23: Evolution of Raman spectra with the degree of order. Summary of observations from reference 81.

2.3.2.2 - Analysis of Raman spectra of Carbon materials

A more thorough interpretation of Raman parameters can be achieved by using G-peak position and
the intensity ratio of D-peak to G-peak “I(D)/I(G)” as order parameters and by distinguishing three
main regions with distinct behavior of such parameters, in what is known as the three stage model of
carbon amorphization from graphite to ta-C (see Figure 2.24). The three stages are as follows:

Stage 1. Graphite ➔ Nanocrystalline graphite (nc-G)

Stage 2. nc-G ➔ a-C

Stage 3. a-C ➔ ta-C (~100% sp³)

Stage 1: In perfect single crystal graphite, carbon atoms are allowed to vibrate in the stretching mode
causing a sharp G-band. However, the breathing mode is prohibited and hence D-band is absent. In
the first transition stage of the model, the single crystalline graphite becomes polycrystalline with increasing number of clusters of size $L_a$. The existence of these irregular clusters adds the freedom to induce the breathing mode of vibration; hence the D-peak appears with continuously increasing intensity. Meanwhile, the G-peak position increases from ~1575 cm$^{-1}$ to ~1600cm$^{-1}$. The $I(D)/I(G)$ increases according to Tunstra and Koeng (TK) equation$^{82}$:

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a}$$

(1)

where $C(\lambda)$ is a coefficient depending on the wavelength of the laser source and can be approximated by the following equation$^{86}$:

$$C(\lambda) = -126 + 0.33(\lambda)$$

(2)

In single crystal graphite $L_a$ is infinitely large, corresponding to $I(D)/I(G)$ of zero. This agrees with the observed spectrum absent a D-peak ($I(D) = 0$).

**Stage 2:** In the second transition stage, further disorder is induced in the form of topological distortions creating deteriorated ring-like configuration with 5, 7 or 8 atoms, and hybridization of some of the sp$^2$ bonds. Clusters get fewer and smaller in size leading to a-C at the end of this stage consisting mainly of sp$^2$ hybridized carbon (20% sp$^3$). In this stage the G-peak position decreases from ~1600cm$^{-1}$ to ~1510cm$^{-1}$ due to softening in the vibrational modes, and the behavior of $I(D)/I(G)$ is opposite to that of the previous stage. Here, it continuously decreases with increasing disorder, making the TK relationship not applicable at this stage. The reason is that cluster size is not important at this stage, due to smaller number of clusters, and hence the D-peak starts to lose its intensity, as the abundance of regions exhibiting the breathing mode decreases. The number of ordered rings is directly proportional to the area of clusters ($L_a^2$). Consequently, $I(D)/I(G)$ can be correlated to $L_a$ using the following relationship;
Stage 3: During the last stage, further hybridization increases the sp\textsuperscript{3} content from \(~20\%\) to 85\%, accompanied by opening of sp\textsuperscript{2} rings and introduction of olefinic carbon chains. This disorder increases the G-peak position from 1510 cm\textsuperscript{-1} to 1570 cm\textsuperscript{-1} as the bonds become shorter in the olefinic chains compared to aromatic rings, leading to higher frequency vibrations\textsuperscript{83}. I(D)/I(G) keeps decreasing in this stage and becomes very low.

In summary, a D-peak can be an indicator of order or disorder depending on the stage at which the structure exists. Increase in D-peak intensity indicates more disorder in graphite as seen in stage 1; it also indicates more order in nanocrystalline and amorphous carbon as seen in stages 2 and 3. As a result, I(D)/I(G) has to be used as a quality indicator of graphene ultrathin films, whereby a high quality ordered sheet results in a lower ratio\textsuperscript{87}. This is also an indirect indication of the sp\textsuperscript{3} content in DLC films, since sp\textsuperscript{3} hybrids are correlated with the degree of disorder in stages 2 and 3 \textsuperscript{84}. Looking
at the three stage model above, it is clear that no unique relationship exists between the G-peak position and the sp$^3$ content in the full range. The variation of the spectral position of the G-peak is useful to determining the state of amorphization of a sample based on its relationship with changes in I(D)/I(G). If the variation in the G-peak position and I(D)/I(G) are directly proportional, then the sample is either at stage 1 or 2. The stage can then be determined by looking at the G-peak position (if less than 1581 cm$^{-1}$, then it is in stage 2). However, if they are inversely related, then this implies the samples are in stage 3. Ultimately when comparing two amorphous carbon films, the highest sp$^3$ content corresponds to the lowest I(D)/I(G) and to the highest G-peak position.

Raman spectra can also be used to identify graphene and to determine the number of layers by using the second order 2D-peak at 2700 cm$^{-1}$. As described in Figure 2.13, the second order peaks appear only in ordered structures of carbon and involve three peaks: 2700 cm$^{-1}$, 2900 cm$^{-1}$ and 3200 cm$^{-1}$. In graphite, the 2900 cm$^{-1}$ peak disappears, while the 2D-peak at 2700 cm$^{-1}$ becomes more intense and splits into two peaks, namely a higher energy sharp peak and a lower energy broad peak with improving ordering of the samples.

The splitting in the 2D-peak also changes as the number of layers in the graphite structure reduces to a single layer. A monolayer sheet of graphene is characterized by a sharp single 2D-peak centered at 2700 cm$^{-1}$ having a width of ~ 24 cm$^{-1}$ 88. Adding more sheets leads to changes in the shape, width and intensity of the peak. In particular, two main types of stacking can be observed for graphene sheets88: the AB-Bernal stacking in which the carbon atoms at the corners of a hexagon in one layer are placed at the vacant centers of a hexagon in another layer and the turbostratic stacking which has random rotational ordering. The shape evolution of the 2D-peak with number of layers can only be observed in the AB stacking, as interlayer coupling between layers affects the phonon modes and electronic structure88 leading to its splitting. Such stacking exists in mechanically exfoliated graphene.

In Bilayer graphene, phonon coupling causes the sharp 2D peak to split into four peaks having a width of ~ 24 cm$^{-1}$, adding one more layer causes the peak to split into six peaks as in trilayer
graphene. After five layers stacked in AB stacking, the 2D-peak shape is not distinguishable from that of graphite where it splits into 2 peaks as mentioned earlier. The intensity of the 2D-peak decreases continuously as the number of layers increases. The I(2D)/I(G) for a single layer graphene in mechanically exfoliated graphene is ~4. However, it is much smaller for single layer graphene obtained by other methods as defects tend to reduce the intensity of the 2D-peak. Solution processed graphene oxide represents such a case, where the peak appears as a very wide low intensity hump.

For turbostratic stacking of graphene layers, the shape of 2D-peak for multilayer graphene is similar to that of a monolayer graphene due to the absence of interlayer coupling; they exhibit larger widths and lower intensities. CVD graphene and solution processed graphene films lie within this category, and identification of the number of layers can be obtained from the relative intensity of the 2D-peak to the G-peak. Single layer solution processed pristine graphene was reported to have I(2D)/I(G) ratio of ~2.1, and the value continuously decreased to about ~0.8 for 4 layers. The same ratio was correlated to number of layers in CVD graphene, where a single layer exhibited a ratio of ~5, reducing to ~2 for two layers and ~0.7 for three layers.
Chapter III

Experimental Methodology
In this chapter, experimental techniques used for sample preparation and characterization are
described, which have been used throughout the remainder of this thesis. Processing systems used to
synthesize the samples will be described along with the specific process parameters. The FCVA
system located in the laboratory of Professor Kyriakos Komvopoulos at the University of California
at Berkeley (UCB) was used for depositing ultrathin DLC films is described\textsuperscript{38}. The CVD furnace in
the laboratory of Professor Norbert Klein was used to deposit graphene layers on copper at the
Imperial College in London (ICL).

The characterization techniques, all of which are available at KAUST, are also presented, including
X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS) and Atomic Force microscopy
(AFM). Data analysis procedures of XPS and RS spectra are presented at the end of this chapter.

\section{Filtered Cathodic Vacuum Arc deposition of DLC thin films}

Deposition of DLC films in this work was achieved by a custom-made FCVA system using a 3D
out-of-plane macroparticle filter and a magnetic field configuration to stabilize the plasma in a dc
arcing mode. In Figure 3.1, the deposition system in both top (a) and side (b) views is shown.

An arc discharge at the cathode between the cathode coil and the upstream coil initiates the plasma
which travels through the filter towards the substrate holder (anode). The four coils in the system
provide magnetic fields in a special configuration designed to enhance the properties of the deposited
film. The cathode coil and upstream coil are responsible for stabilizing the dc arc discharge of the system (see Figure 3.2). By acting in opposing directions, the magnets generate a cusp at the anode and provide a continuous flow of electrons from the cathode, which is crucial to achieve a stable arc current.

The upstream, auxiliary and downstream coils all operate at their peak values to provide intense magnetic fields acting in the same direction along the 3D out-of-plan duct to drive and guide the electrons and ionic species towards the substrate. The out-of-plane configuration of the filter introduces more directional changes to the particulates in the plasma, leading to higher efficiency filtering of the plasma. Arcing of a graphite cathode produces a plasma of carbon species with a very high flux of $1.48 \times 10^{19}$ ions/m$^2$s by using a 70 A arc discharge current.

The system is also equipped with a 64 mm Kaufman ion source used for substrate cleaning by Argon sputtering prior to deposition. High vacuum in the chamber is maintained below $3 \times 10^{-7}$ torr by using a cryogenic pump.

Uniform deposition is made possible by continuous substrate rotation during deposition. The tilt angle of the holder can also be controlled to provide a wide range of deposition angles, enabling the investigation of deposition angle effect on the structure of DLC films. The deposition angle is
defined in reference to the deposition axis (see Figure 3.3), whereby $\theta = 90^\circ$ corresponds to normal incidence deposition.

![Diagram of etching and deposition angles](image)

*Figure 3.3: References of (a) etching and (b) deposition angles.*

Deposition of ultrathin DLC films was achieved at a discharge of 24 V maintained at a current of 70 A, producing a carbon ion flux of $1.48 \times 10^{15}$ ions/cm$^2$ s. The substrate was pulse biased with a frequency of 25 kHz and an average bias of -100 V. Thin films were deposited on 4” diameter Si(100) wafers, which were sputter-cleaned by Ar$^+$ ion beam of 500 eV and 16 mA, for 2 minutes at $60^\circ$ incidence angle. The substrate holder was rotated at 60 RPM both during deposition and cleaning.

### 3.2 - Chemical vapor deposition (CVD) of graphene

The CVD system used in this work is a hot wall furnace LPCVD system shown in Figure 3.4. It consists of an electrically powered cylindrical furnace with a quartz tube (diameter of 3.6 cm and 100 cm in length) placed at its center. The temperature of the furnace was monitored and controlled by a proportional integrated differential (PID) controller (Eurotherm 2204) with the thermocouple (TC) installed near the center of the furnace. A rotary pump was used to achieve a base pressure of $1 \times 10^{-3}$ mbar. The pressure of the system was monitored using a pinning gauge (Leybold PTR90) and controlled through a needle valve attached to the inlet of the pump. Cylinders of CH$_4$, H$_2$ and Ar
were attached to the furnace and the gas flow in the system was controlled by mass flow controllers. 
Cu foils used in this work were placed at the center of the cylindrical furnace. Cooling of the system occurred naturally by turning off the power supply as the cooling rate was shown not to affect the growth of graphene.

Figure 3.4: Schematic representation of the CVD system used for graphene deposition on copper foil.

3.3 – Radio frequency plasma oxidation

Oxidation of graphene was carried out by exposing the samples to radio frequency plasma of oxygen gas. A PDC-32-2 plasma cleaner from Harrick plasma was used, equipped with PDC-FMG-2 PlasmaFlo to control and measure the flow of gases into the chamber. The cylindrical chamber is 3 inches in diameter and 6.5 inches deep. A vacuum was generated by an Oerlikon Trivac E2 pump, achieving a base pressure of ~ 13 mTorr. The system provides RF frequency in the range of MHz controlled by the power applied which can be set to either low (6.8 W), medium (10.5 W) and High (18 W). In this work, plasma treatment of graphene was applied with medium power (10.5 W) at oxygen-filled chamber pressure of ~ 40 mTorr for all samples. An increase in chamber pressure was observed after plasma ignition up to ~ 50 mTorr.
3.4 - X-ray photoelectron spectroscopy (XPS)

3.4.1 – System specification and measurement parameters

XPS studies in this project were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under $1.0 \times 10^{-9}$ Torr vacuum. Measurements were performed in hybrid mode using electrostatic and magnetic lenses. All spectra were recorded using an aperture slot of 300 μm x 700 μm. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 80 and 20 eV, respectively.

Both DLC films and CVD graphene in this work were examined by XPS, looking into the C 1s peak to find the relative sp³ and sp² hybridizations as well as the concentration of various other elements in the samples.

3.4.2 - Data analysis and peak fitting

The C 1s peaks for both DLC films and Graphene were deconvoluted into 6 peaks and 5 peaks, respectively, using CASAXPS software, as shown in Figure 3.5. The fitted lineshape combines both Gaussian and Lorentzian functions with a ratio of 70% to 30%, respectively. The peaks and their identification were described in section 2.3.1.

For DLC films, the peaks were fitted with fixed FWHM, leaving the position to vary at a specific range around the expected values, whereas for graphene samples the peaks were fitted with different FWHM and the peak position was restricted within an expected range, while the FWHM was allowed to vary. Figure 3.5 shows a typical fitting of the high resolution C 1s peak of a DLC film and CVD graphene.
Figure 3.5: Fitting of high-resolution C 1s peak for (a) DLC film deposited at 50° and -100 V for 30 seconds, and (b) as-deposited CVD graphene sample.

3.5 - Raman Spectroscopy (RS)

3.5.1 – System specification and measurement parameters

RS measurements were performed using two different systems. LabRAM ARAMIS was used to characterize DLC films using an excitation source of 473 nm, whereas LABRAM HR was used to characterize the graphene samples with an excitation source of 533 nm. In both systems a 0.5 mW laser was focused with a 100x objective to form a spot size of 1 µm. The scattered signal was dispersed with a 1800 1/mm or 600 1/mm grating for DLC and graphene sample respectively, and collected in a backscattering geometry in all cases. The choice of instrument was made based on non-
technical considerations, such as availability. The collection range and acquisition time were optimized depending on the type of samples characterized, and are summarized in table 3.1. The increased acquisition time for DLC films compared to graphene is due the low signal-to-noise ratio of the former.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectral range (cm$^{-1}$)</th>
<th>Acquisition time (seconds)</th>
<th>Repetition</th>
<th>Scanned points on sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC films</td>
<td>1100 – 2000</td>
<td>100</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Graphene</td>
<td>1100 – 3000</td>
<td>10</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

3.5.2 - Data analysis and peak fitting

The Raman spectra were analyzed using Origin© software. The analysis process includes a spectral correction step and fitting to identify and quantify the various peaks.

A typical spectrum of a DLC film sample is shown in Figure 3.6a. It shows a single broad peak centered around 1500 cm$^{-1}$, which is a common feature for amorphous carbons where the G-peak and D-peak merge together. The spectrum includes instrumental background and some very sharp peaks representing noise. Such features must be removed as they interfere with the parameters to be obtained from peak fitting. Spectral correction process should remove any contribution from the substrate and instrumental background. A sharp feature at 1550 cm$^{-1}$ appeared in almost all of the samples and is related to atmospheric oxygen; it was removed before the fitting process to improve the fitted peaks. The correction process is illustrated in Figures 3.6b through 3.6e; starting with subtracting the Si(100) substrate spectrum collected at the same parameters; this step is necessary since silicon has a prominent feature at 1450 cm$^{-1}$ that can interfere with the DLC features$^{35}$, as shown in Figure 3.6b. A baseline correction shown in Figure 3.6d removes instrumental background and provides better fitting of the spectrum.

The resulting corrected spectrum is shown in Figure 3.6e, which can be accurately fitted into the corresponding D and G peaks.
Figure 3.6: Spectral correction process. (a) Raw spectrum exhibiting noise peaks and oxygen peak at 1550 cm\(^{-1}\), (b) silicon subtraction from the spectrum, removal of the oxygen and noise peaks yielding (c). (d) Baseline correction to remove instrumental background leading to the spectrum in (e).

The corrected spectra were then deconvoluted into their respective components using the curve fitting feature of the software. All the peaks were fitted with two Gaussian line-shaped peaks appearing at \(\sim 1560 \text{ cm}^{-1}\) and \(\sim 1380 \text{ cm}^{-1}\) and representing the G- and D-peaks, respectively. However, some spectra revealed features from the silicon substrate near 1450 cm\(^{-1}\) even after the subtraction process; it was therefore necessary to use a third Gaussian peak at that position to provide accurate fitting for the D and G peaks as shown in Figure 3.7.

Figure 3.7: Peak fitting of corrected Raman spectra, using (a) 2 Gaussian peaks corresponding to D and G peaks, and using (b) 3 Gaussian peaks due to the presence of residual silicon peak even after subtraction.

The G-peak and D-peak positions and intensities were deduced from the fitted peaks, and \(I(D)/I(G)\) was subsequently calculated for all samples. Values used were averaged from three points on each sample.
Spectra of as-deposited and oxidized CVD graphene were acquired similarly. Raman spectra were collected from 7 different points followed by baseline correction and peak fitting. Instrumental background was removed by an 8th degree polynomial base line using LabSpec© software, followed by fitting all the peaks using the Lorentzian lineshape in Origin©. Four main Lorentzian peaks were used in the fitting process, including the D-peak at ~1350 cm⁻¹, G-peak at ~1580 cm⁻¹, 2D-peak at ~2700 cm⁻¹ and D'-peak at ~1620 cm⁻¹. Another peak that appeared occasionally at ~1550 cm⁻¹ was also used to improve fitting. All fit parameters were averaged over the 7 spectra of each sample before further analysis.

3.6 – Atomic Force Microscopy

The topography and surface structure were examined by atomic force microscopy in tapping mode. AFM images the topography of material surfaces using a physical probe that scans the sample. The probe consists of a cantilever and a very sharp tip. Changes in the surface topography cause the cantilever to bend up or down depending on the height encountered and the stiffness of the cantilever. Changes in cantilever curvature are detected through a focused laser that changes the position of the reflected beam on a photodetector. The collected variations are transferred into maps of the surface. AFM allows determination of surface roughness, surface morphology and even the thickness of the sample in some cases. All AFM images were taken using Agilent 5400 SPM/AFM microscope, operating in tapping mode. Nanosensors silicon tips with frequency of 300 Hz were used in all experiments, using a scan speed of 0.8 lines/second and a resolution of 512 points per line.
Chapter IV

Structural analysis of diamond-like carbon over-coats for magnetic hard drive applications
Diamond-like carbon is an essential overcoat material in magnetic storage devices. It is responsible for protecting both the magnetic layer and the read/write head from corrosion and mechanical wear. To be effective, the overcoat must be continuous, uniform and exhibit sufficient mechanical strength and toughness via large sp³ fraction, while fulfilling the requirement of being ultrathin. It is estimated that a carbon overcoat thickness of ~ 1 nm - 2 nm is required to achieve storage density of 1 Tbits/in². Unfortunately, sputtered a-C coatings currently in use by industry do not meet these requirements, failing to provide continuous coverage at such small thicknesses. Filtered cathodic vacuum arc deposition has been shown to deposit ultrathin continuous DLC overcoats with sp³ fraction approaching 50%, as reviewed in Chapter 2. In this chapter, the influence of deposition angle and deposition time on the structure and morphology of FCVA-deposited DLC films is evaluated, identifying the optimal conditions that satisfy the requirements of uniformity, smoothness and maximum sp³ content.

### 4.1 - Analysis objectives

1. Evaluate the sp³ content for DLC films deposited by FCVA at different deposition angles and deposition times using RS and XPS.
2. Investigate the surface topography of these films to determine surface roughness and uniformity of coverage by using AFM.

![Experimental approach for analysis of DLC films deposited by the FCVA technique.](image)
4.2 - Sample preparation

DLC films investigated in this chapter were deposited using a custom-made FCVA system described in section 3.1. Si (100) substrates were placed at the sample holder and etched for 2 minutes by Argon ion beam at an incidence angle of 60° to provide a clean surface for carbon deposition. Two graphite cathodes were used throughout this project. The corresponding samples will be labeled with an “o” for old cathode and “n” for the new cathode.

Samples with a range of deposition angles from 50° to 90° incidence were synthesized using a fixed deposition time of 30 seconds and fixed substrate bias of -100 V. Additional samples were prepared with deposition times of 6, 30, 60 and 120 seconds at fixed deposition angles of 70° or 90° with or without applying a substrate bias. In Table 4.1, the various samples prepared for this study are summarized and the characterization methods that have been applied to them.

4.3 - Results

4.3.1 - Raman Spectroscopy

As presented in section 2.3.2, parameters deduced from Raman spectra of DLC thin films provide valuable information about its structure. The sp³ content can be qualitatively determined by using the ratio of the intensity of the D-peak to the intensity of the G-peak I(D)/I(G), since it is inversely related to the sp³/sp² in amorphous carbon. The variation in the G-peak position can be used to identify the amorphization stage of the sample in terms of the three stage model presented in section 2.3.2. If the G-peak position is directly related to the I(D)/I(G) variation, then the sample is undergoing nc-G→a-C transition (stage 2), and the sp³ content is lower. An inverse relation, however, indicates a sample undergoing a-C→ta-C transition (stage 3). DLC films should exist in the third transition stage.
Table 4.1: List of samples prepared and analyzed along with deposition conditions and characterization methods used.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Deposition angle (°)</th>
<th>Deposition time (sec)</th>
<th>Bias (V)</th>
<th>Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-D90-B100-o</td>
<td>90</td>
<td>30</td>
<td>-100</td>
<td>XPS, RS, AFM</td>
</tr>
<tr>
<td>Si-D80-B100-o</td>
<td>80</td>
<td>30</td>
<td>-100</td>
<td>XPS, RS, AFM</td>
</tr>
<tr>
<td>Si-D70-B100-o</td>
<td>70</td>
<td>30</td>
<td>-100</td>
<td>XPS, RS, AFM</td>
</tr>
<tr>
<td>Si-D60-B100-o</td>
<td>60</td>
<td>30</td>
<td>-100</td>
<td>XPS, RS, AFM</td>
</tr>
<tr>
<td>Si-D50-B100-o</td>
<td>50</td>
<td>30</td>
<td>-100</td>
<td>XPS, RS, AFM</td>
</tr>
<tr>
<td>Si-D90-0V-6s-n</td>
<td>90</td>
<td>6</td>
<td>0</td>
<td>RS, AFM</td>
</tr>
<tr>
<td>Si-D90-0V-30s-n</td>
<td>90</td>
<td>30</td>
<td>0</td>
<td>RS, AFM</td>
</tr>
<tr>
<td>Si-D90-0V-60s-n</td>
<td>90</td>
<td>60</td>
<td>0</td>
<td>RS, AFM</td>
</tr>
<tr>
<td>Si-D90-0V-120s-n</td>
<td>90</td>
<td>120</td>
<td>0</td>
<td>RS, AFM</td>
</tr>
<tr>
<td>Si-D90-100V-6s-n</td>
<td>90</td>
<td>6</td>
<td>-100</td>
<td>RS</td>
</tr>
<tr>
<td>Si-D90-100V-30s-n</td>
<td>90</td>
<td>30</td>
<td>-100</td>
<td>RS, AFM</td>
</tr>
<tr>
<td>Si-D90-100V-60s-n</td>
<td>90</td>
<td>60</td>
<td>-100</td>
<td>RS, AFM</td>
</tr>
<tr>
<td>Si-D90-100V-120s-n</td>
<td>90</td>
<td>120</td>
<td>-100</td>
<td>RS</td>
</tr>
<tr>
<td>Si-D70-100V-6s-n</td>
<td>70</td>
<td>6</td>
<td>-100</td>
<td>RS</td>
</tr>
<tr>
<td>Si-D70-100V-30s-n</td>
<td>70</td>
<td>30</td>
<td>-100</td>
<td>RS</td>
</tr>
<tr>
<td>Si-D70-100V-60s-n</td>
<td>70</td>
<td>60</td>
<td>-100</td>
<td>RS</td>
</tr>
<tr>
<td>Si-D70-100V-120s-n</td>
<td>70</td>
<td>120</td>
<td>-100</td>
<td>RS</td>
</tr>
</tbody>
</table>

**Influence of deposition angle**

In Figure 4.2, Raman spectra of samples fabricated with different deposition angles are presented. Variation of I(D)/I(G) and G-peak position extracted from the spectra obtained with respect to deposition angle are shown in Figure 4.3. I(D)/I(G) dips and then rises passing a minimum at 70°. Meanwhile, the G-peak position remains unchanged at first, rising rapidly for deposition angles of 70° and above.
A lower $I(D)/I(G)$ indicates a more disordered sample with respect to $sp^2$ bonds and increased $sp^3$ content, as in amorphous carbon. The highest degree of $sp^2$ disorder is observed at $70^\circ$ deposition angle meaning that films deposited at this angle are expected to exhibit the highest $sp^3/sp^2$ ratio.

Comparing G-peak position and $I(D)/I(G)$ behavior helps to define the stage of amorphization. A direct relation is observed between the G-peak position and $I(D)/I(G)$ when the deposition angle is increased from $50^\circ$ to $60^\circ$, confirming that the structure of the film lies within stage 2 ($nc-G\rightarrow a-C$) of the three stage model. The two parameters vary inversely at deposition angles larger than $60^\circ$ up to $80^\circ$, indicating that samples deposited within this range lie in stage 3 ($a-C\rightarrow ta-C$) of the three stage model.
model. Deposition between 80° and 90° exhibits a direct relation, indicating that samples deposited within this range of deposition angles are in stage 2 (nc-G\(\rightarrow\)a-C).

Samples with structures lying within stage 2 in the three stage model (nc-G\(\rightarrow\)a-C) exhibit a very low sp\(^3\) content (up to 20%), and disorder in this stage is mainly caused by distortion in sp\(^2\) bonded carbon rather than sp\(^3\) hybridization. Samples deposited in the range of 50° to 60° exhibit structures within this stage. Deposition angles between 60° and 80° in Figure 4.3 represents the range of deposition angles that would achieve high sp\(^3\) contents ranging between 20% and 85%, since they lie within stage 3 of the three-stage model.

Raman analysis of the influence of deposition angle indicates that deposition angle should be at least 60° for FCVA to achieve ta-C thin films with a significant amount of sp\(^3\) bonding. The highest sp\(^3\) content was found at a deposition angle of 70°.

**Influence of deposition time**

In Figure 4.4, Raman spectra for FCVA depositions lasting 6, 30, 60, and 120 s at incidence angles of 90° and 70° are presented. The evolution of I(D)/I(G) and G-peak position as a function of deposition time are summarized in Figure 4.5.

The growth behavior at both angles appears similar; I(D)/I(G) decreases significantly when the deposition time increases from 6 to 30 s, after which it stabilizes and continues to decrease with a much lower rate. The position of the G-peak generally increases with prolonged deposition time, varying in the range from 1537 cm\(^{-1}\) to 1560 cm\(^{-1}\).
Figure 4.4: Raman spectra of DLC films deposited at (a) 90° and (b) 70° with a substrate bias of -100 V and for increasing deposition times.

Increasing deposition time therefore promotes structural transitions from a-C towards ta-C, as implied by the inverse relationship between G-peak position and I(D)/I(G). This can be explained by deposition of more material with increasing time and increased ion bombardment fluence, which promotes sp³ hybridization.
Figure 4.5: Variation of (a) I(D)/I(G) and (b) G-peak position with deposition time at fixed deposition angles of 70 and 90° and a substrate bias of -100V. The sample prepared at 70° with 6 s deposition time is omitted as the spectrum was too noisy.

Influence of substrate bias

Raman spectra of DLC films deposited on unbiased substrate at 90° are shown in Figure 4.6. In Figure 4.7, I(D)/I(G) and G-peak position for unbiased and biased depositions performed at 90° incidence angle are compared. I(D)/I(G) of the biased samples generally falls below that of the unbiased substrate, indicating a higher sp³ content when a substrate bias is applied. This is due to the fact that biasing induces ion bombardment with mean ion energy of 120 eV, whereas unbiased conditions are limited to C ion bombardment with intrinsic ion energy of 19 eV. These results agree with previous findings of the influence of substrate bias\textsuperscript{35,43,37}. 

---

The diagrams show the variation of I(D)/I(G) and G-peak position with deposition time at fixed angles of 70° and 90°. The graph for I(D)/I(G) indicates a decrease with increasing deposition time, with the 90° sample showing a steeper decline compared to the 70° sample. Similarly, the G-peak position shows an increase with deposition time, again with the 90° sample having a higher peak position compared to the 70° sample. The data points for 6 s deposition at 70° are not included due to the noisy spectrum.
Figure 4.6: Raman spectra of DLC films deposited at 90° without substrate biasing with increasing deposition time.

Figure 4.7: Variation of (a) I(D)/I(G) and (b) G-peak position with deposition time for samples deposited at 90° with 0 and -100 V biasing conditions.
4.3.2 - X-ray Photoelectron Spectroscopy:

XPS analysis allows quantification of the sp³ and sp² contents of the DLC films, as detailed in chapters 2 and 3. Figure 4.8 shows the fitted C 1s peaks for samples deposited at various deposition angles. The breakdown of C 1s-3(sp³) and C 1s-2(sp²) peaks can be seen in Figures 4.8a through 4.8e, along with details of other peaks. Increasing deposition angle is accompanied with an increase in sp³ content and decrease in sp² content; all other peaks appear to decrease only slightly.

Table 4.2 shows the fitted peaks positions and FWHM within the C 1s peak for different deposition angles.

Table 4.2: C 1s peak fitting parameters for each deposition angle

<table>
<thead>
<tr>
<th>Deposition angle</th>
<th>C 1s-1 (sp1)</th>
<th>C 1s-2 (sp2)</th>
<th>C 1s-3 (sp3)</th>
<th>C 1s-4</th>
<th>C 1s-5</th>
<th>C 1s-6</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°</td>
<td>283.3</td>
<td>284.5</td>
<td>285.3</td>
<td>286.6</td>
<td>287.7</td>
<td>288.9</td>
<td>1.17</td>
</tr>
<tr>
<td>60°</td>
<td>283.0</td>
<td>284.5</td>
<td>285.2</td>
<td>286.5</td>
<td>287.6</td>
<td>288.9</td>
<td>1.12</td>
</tr>
<tr>
<td>70°</td>
<td>283.3</td>
<td>284.5</td>
<td>285.3</td>
<td>286.6</td>
<td>287.7</td>
<td>288.9</td>
<td>1.09</td>
</tr>
<tr>
<td>80°</td>
<td>282.9</td>
<td>284.4</td>
<td>285.1</td>
<td>286.5</td>
<td>287.6</td>
<td>288.8</td>
<td>1.08</td>
</tr>
<tr>
<td>90°</td>
<td>283.0</td>
<td>284.4</td>
<td>285.1</td>
<td>286.5</td>
<td>287.6</td>
<td>288.8</td>
<td>1.08</td>
</tr>
</tbody>
</table>

The relative content of each peak is measured by dividing the corresponding area over the total area of the C 1s peak; the calculated values are presented in table 4.3 and plotted in Figure 4.9. Significant changes are observed in both sp² and sp³ content when increasing the deposition angle from 50° to 60°. The sp² content decreases from 55% to 43% while sp³ bonded carbon increases from 26% to 42%. Further increase of the deposition angle maintains the same trend but with a much reduced rate of increase of sp³ up to 46.5%, while sp² content remains nearly unchanged, hovering around 41%.

Table 4.3: Relative area of various peaks in percentage (%) normalized to the total area of the C 1s peak.

<table>
<thead>
<tr>
<th>Deposition angle</th>
<th>C 1s-1</th>
<th>C 1s-2</th>
<th>C 1s-3</th>
<th>C 1s-4</th>
<th>C 1s-5</th>
<th>C 1s-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°</td>
<td>3.3</td>
<td>55.8</td>
<td>26.3</td>
<td>7.7</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td>60°</td>
<td>1.7</td>
<td>43.0</td>
<td>42.8</td>
<td>7.1</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>70°</td>
<td>1.8</td>
<td>41.0</td>
<td>44.8</td>
<td>6.7</td>
<td>2.9</td>
<td>2.8</td>
</tr>
<tr>
<td>80°</td>
<td>1.4</td>
<td>40.7</td>
<td>46.5</td>
<td>6.3</td>
<td>2.7</td>
<td>2.4</td>
</tr>
<tr>
<td>90°</td>
<td>1.3</td>
<td>40.8</td>
<td>46.5</td>
<td>6.3</td>
<td>2.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Figure 4.8: High resolution C 1s peak with fitting for samples prepared at deposition angles of (a) 50°, (b) 60°, (c) 70°, (d) 80°, (e) 90°. All depositions lasted 30 s and were performed at a substrate bias of -100 V.

Figure 4.9: Variation of sp² and sp³ contents in DLC films prepared with varying deposition angles as obtained from XPS. All depositions lasted 30 s and were performed at a substrate bias of -100 V.
The variation of sp³/sp² ratio with deposition angle is shown in Figure 4.10. The most significant increase of sp³/sp², from 0.47 to 0.99, is observed when increasing deposition angle from 50 to 60°. The ratio continues to rise with increasing incidence angle and plateaus at a value of 1.4 for incidence angles of 80° and above. XPS results confirm quantitatively the observation made based on Raman spectroscopy that increasing the deposition angle towards normal incidence results in increase of sp³ content, with the most significant difference observed between 50° and 60°. This suggests that deposition angles below 60° are not suitable for inducing sp³ hybridization required for coating magnetic recording media.

4.3.3 - Atomic Force Microscopy:

The surface topography and root-mean-square (RMS) roughness of the deposited films were examined by AFM. Figure 4.11 reveals a gradual change in topography as the deposition angle increases. Depositions performed at 50°, 60° and 70° appear to produce smoother surfaces, whereas approaching normal incidence deposition leads to appearance of island-like features. Horizontal profiles and RMS surface roughness values of samples prepared on biased substrate are plotted in Figures 4.12 and 4.13, respectively, confirming this trend. AFM images of DLC films deposited at 90° for 6 seconds and 2 minutes on unbiased substrate are shown in Figures 4.14a and 4.14b,
respectively. Images of films deposited at 90° for 30 seconds and 1 minute on biased substrate are shown in Figures 4.15a and 4.15b, respectively.

Figure 4.11: AFM micrographs of DLC films prepared with varying deposition angles of (a) 50°, (b) 60°, (c) 70°, (d) 80° and (e) 90°. All depositions lasted 30 s and were performed at a substrate bias of -100 V.
The RMS surface roughness with increasing deposition time at normal incidence angle for unbiased conditions is plotted in Figure 4.16. It reveals that significant roughening occurs during deposition at 90°. The RMS roughness of the unbiased conditions ranged between 0.17 nm and 0.22 nm, while for the biased conditions it took values between 0.2 nm and 1 nm.

Figure 4.12: Horizontal line profiles along the lines shown in figure 4.11 for various deposition angles. All depositions lasted 30 s and were performed at a substrate bias of -100 V.

Figure 4.13: RMS roughness variation with increasing deposition angle for samples deposited for 30 s at a substrate bias of -100 V.
Figure 4.14: AFM images of DLC films deposited at 90° without substrate biasing for (a) 6 seconds and (b) 2 minutes.

Figure 4.15: AFM images of DLC films deposited at 90° with substrate biasing for (a) 30 seconds and (b) 1 minute.
4.4 - Discussion

The most relevant RS and XPS results - I(D)/I(G) and sp³/sp² - are presented in Figure 4.17. Both plots reveal a minimum angle of 60° is necessary to achieve sufficient sp³ content. The continuously increasing sp³ content with deposition angle as concluded from XPS, indicates that C⁺ ion bombardment at normal incidence is more effective at transforming sp² bonds to sp³. This is most likely due to more effective momentum and energy transfer to surface and sub-surface atoms when approaching normal incidence conditions.

By contrast, deposition at low angles such as 50° and 60° has a larger in-plane moment component which is unlikely to participate in the production of sp³ hybridized bonds.

The observed increase in the I(D)/I(G) ratio for deposition angles of 80° and 90° could be interpreted as a reduction in sp³ content in the sample, which appears to be contradicted by XPS results. However, I(D)/I(G) could be sensing other types of disorder in the sample. Here, it is useful to emphasize that visible RS does not detect the sp³ content directly. Instead, it relies on correlation with I(D)/I(G). The appearance of island-like morphological features on the surface of samples deposited at 80° and 90°, and the associated important rise in RMS surface roughness appears to
correlate well with the reversal of I(D)/I(G) as shown in Figure 4.18. This may provide an alternative explanation as to the increasing ratio despite increasing sp³ content confirmed by XPS.

![Figure 4.18: Variation of I(D)/I(G) and RMS roughness with increasing deposition angle. All depositions lasted 30 s and were performed at a substrate bias of -100 V.](image)

Importantly, considering the surface roughness and sp³ content evolutions with deposition angle suggests that a deposition angle of 70° is optimal for ta-C film formation from within the parameter space so-far explored.

The deposition time is another important parameter to tune. Increasing deposition time leads to increased sp³ content as more material and energy are deposited onto the substrate surface via ion bombardment. However, increasing deposition time comes at the expense of increasing thickness and surface roughness which are not desirable for hard drive applications. Raman spectral analysis further indicates that sufficiently high sp³ hybridization is achieved at 30 seconds, so that 30 seconds are sufficient to form ta-C films suitable for hard drive application.
Chapter V

Structural and chemical evolution of O₂ plasma-treated Graphene
Oxidation of graphene has been recently investigated for two main reasons. Partially oxidized graphene has been shown to exhibit luminescence\textsuperscript{75} and semiconducting\textsuperscript{76} properties, which expands the applications in which graphene sheets can be used. Oxidized graphene is also a form of CDG that is actively pursued as a main route to obtain ultrathin films of graphene via solution processing and subsequent reduction into graphene. However, graphene oxide sheets cannot be fully reduced, as residual defects and oxygen remain even after the reduction process. Understanding the oxidation mechanism may provide better control of the properties of partially oxidized graphene, as well as suggest more efficient reduction methods to approach the properties of pristine graphene.

This chapter investigates plasma oxidation of CVD graphene formed on copper foil. This is done by monitoring the changes in the structure of graphene by RS, XPS and AFM throughout the oxidation process.

5.1 – Analysis Objectives

- Investigate the structural and chemical evolution of CVD graphene films as a function of oxidation time
- Provide a descriptive model for the mechanism of graphene oxidation

5.2- Sample synthesis

Graphene on copper foil was fabricated using the CVD system described in chapter 2. During heating stage, the flow rate of H\textsubscript{2} gas was 5 sccm. After annealing with the same H\textsubscript{2} flow rate for 30 min, CH\textsubscript{4} was introduced to the furnace at the flow rate of 0.5 sccm during the growth stage (growth pressure = 0.2 mbar). After the growth time of 30 min, methane gas was shut off and the furnace was allowed to cool down naturally with hydrogen flow of 5 sccm.
5.3 - Results

5.3.1 – Characterization of as-deposited CVD graphene

Identification and characterization of the pristine CVD graphene sample was done by RS and XPS. A typical Raman spectrum of the as-deposited sample is shown in Figure 5.1, whereas Table 5.1 summarizes the fitted peak positions, intensities and the corresponding ratios. The characteristic 2D-peak appears as a sharp intense Lorentzian peak at ~2660 cm\(^{-1}\) along with G-peak and a very low intensity D-peak. Average value of I(2D)/I(G) for as-deposited samples is ~ 2.3, which indicates along with an average FWHM of ~38 cm\(^{-1}\) that the sample consists mainly of single or bilayer sheets\(^{36,56}\).

![Raman spectrum](image)

**Figure 5.1: Typical Raman spectrum obtained for as-deposited CVD graphene.**

The appearance of the D-peak is likely due to presence of edges or grain boundary defects in the graphene layer. Since it only appeared when scanning certain locations of the sample, it is most likely associated to edge and grain boundary effects.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Position (cm(^{-1}))</th>
<th>Width (cm(^{-1}))</th>
<th>Intensity (cts)</th>
<th>I(D)/I(G)</th>
<th>I(2D)/I(G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G – Peak</td>
<td>1580.2</td>
<td>20.1</td>
<td>4202</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D – Peak</td>
<td>2663.2</td>
<td>35.9</td>
<td>9638</td>
<td>0.13</td>
<td>2.29</td>
</tr>
<tr>
<td>D – Peak</td>
<td>1333.7</td>
<td>18.6</td>
<td>554</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Graphene cluster size can be estimated using the TK equation described in section 2.3.2 and the I(D)/I(G) ratio averaged over seven points on the sample. Since the laser source used had a wavelength of 532 nm, C(532) was estimated to be 50 Å. A cluster size for the as-deposited sample is therefore estimated to be 380 Å. The size of graphene crystallites is smaller than the size of the RS laser spot (1µm), which makes it likely to observe scan-to-scan variations of the D-peak as the likelihood of the laser probing very different numbers of grain boundary defects from one scan is very high.

Figure 5.2 shows the C 1s peak of pristine graphene fitted with five peaks, two of which represent carbon-carbon bonding, and the other three are due to different states of carbon-oxygen bonds.

As-deposited graphene sample was observed to exhibit a large sp³ content of about 36 % (see Figure 5.8), whereas pristine graphene deposited by CVD is expected to have little if any sp³ hybridized carbon. Such large content may be due to the presence of C-H bonding. The deposition chamber was filled with H₂ at temperatures up to 1000°C before introducing methane; hence residual hydrogen at the surface of Cu or in the gas phase may react with the growing graphene film to hydrogenate it. However, this remains speculative and needs to be investigated further.

**Figure 5.2: High-resolution C 1s peak with fitting for as-deposited graphene sample.**

5.3.2- Graphene Oxidation
Graphene samples were oxidized by radio frequency oxygen plasma by placing the samples in the plasma reactor described in section 3.3. The degree of oxidation was controlled by varying the exposure time, keeping all other parameters constant, as shown in Table 5.2.

<table>
<thead>
<tr>
<th>Table 5.2: Plasma oxidation conditions for graphene samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD graphene</td>
</tr>
<tr>
<td>Duration</td>
</tr>
<tr>
<td>Base pressure (mTorr)</td>
</tr>
<tr>
<td>Oxygen (O\textsubscript{2}) pressure (mTorr)</td>
</tr>
<tr>
<td>Process pressure (mTorr)</td>
</tr>
</tbody>
</table>

5.3.3 - X-ray photoelectron spectroscopy (XPS)

The influence of plasma oxidation is best understood by measuring the oxygen content and nature of carbon-oxygen bonds as a function of plasma exposure time using XPS, as seen in Figure 5.3 for the C 1s peak. The spectra consist mainly of two peaks, one of which is centered at 284.5 eV, while the other is located at 288.5 eV. Both peaks appear to undergo broadening and a red shift with increasing exposure time.

![Figure 5.3: Evolution of C 1s peak with oxygen plasma exposure time.](image)

Table 5.3 shows the various peaks and parameters used in the fitting process. In Figure 5.4 the fitted peaks of plasma-oxidized graphene samples are shown. The oxygen related peaks appear to increase
in area with prolonged exposure time, indicating an increase of oxygen species in the sample, whereas carbon-related peaks behave in an opposite way. The sp² peak diminishes while the sp³ peak develops with larger exposure time.

The relative content of the various species and their evolution with plasma exposure time were calculated by dividing the area of the peak corresponding to certain species divided by the overall area of the C 1s peak. In Table 5.4, the numerical results of the relative area in percent for all 5 peaks of pristine and plasma oxidized samples are shown. The total oxygen fraction is calculated by adding up all three oxygen related peaks.

Table 5.3: Deconvoluted C 1s peak positions and FWHM (in parentheses) for increasing oxygen plasma exposure times.

<table>
<thead>
<tr>
<th>Oxidation time</th>
<th>As-Deposited</th>
<th>1s</th>
<th>3s</th>
<th>5s</th>
<th>10s</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C (Sp²)</td>
<td>284.4 (0.82)</td>
<td>284.3 (0.74)</td>
<td>284.3 (0.80)</td>
<td>284.3 (0.80)</td>
<td>284.3 (0.85)</td>
</tr>
<tr>
<td>C-C (Sp³)</td>
<td>284.9 (1.29)</td>
<td>284.9 (1.08)</td>
<td>285.1 (1.00)</td>
<td>284.9 (1.17)</td>
<td>285.1 (1.27)</td>
</tr>
<tr>
<td>C=O</td>
<td>286.3 (1.26)</td>
<td>286.1 (1.39)</td>
<td>286.1 (0.85)</td>
<td>286.1 (1.36)</td>
<td>286.2 (1.35)</td>
</tr>
<tr>
<td>C=O</td>
<td>287.2 (1.32)</td>
<td>287.3 (1.39)</td>
<td>286.9 (1.21)</td>
<td>286.9 (0.92)</td>
<td>287.0 (1.09)</td>
</tr>
<tr>
<td>O=O=C-O</td>
<td>288.5 (1.39)</td>
<td>288.7 (1.35)</td>
<td>288.5 (1.39)</td>
<td>288.6 (1.37)</td>
<td>288.7 (1.39)</td>
</tr>
</tbody>
</table>

Table 5.4: Relative area (%) of various C 1s peaks for various oxygen plasma exposure times

<table>
<thead>
<tr>
<th>Samples</th>
<th>C-C(sp²)</th>
<th>C-C(sp³)</th>
<th>C=O</th>
<th>C=O</th>
<th>O=C-O</th>
<th>Total oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>47.7</td>
<td>36.3</td>
<td>7.5</td>
<td>1.7</td>
<td>6.9</td>
<td>16.1</td>
</tr>
<tr>
<td>1 second</td>
<td>48.8</td>
<td>35.2</td>
<td>9.2</td>
<td>1.6</td>
<td>5.3</td>
<td>16.0</td>
</tr>
<tr>
<td>3 seconds</td>
<td>56.3</td>
<td>23.3</td>
<td>5.0</td>
<td>5.0</td>
<td>10.4</td>
<td>20.5</td>
</tr>
<tr>
<td>5 seconds</td>
<td>23.8</td>
<td>48.3</td>
<td>13.3</td>
<td>2.5</td>
<td>12.1</td>
<td>27.9</td>
</tr>
<tr>
<td>10 seconds</td>
<td>5.8</td>
<td>70.9</td>
<td>10.4</td>
<td>1.8</td>
<td>11.1</td>
<td>23.3</td>
</tr>
</tbody>
</table>
C 1s 1: C-C sp²
C 1s 2: C=C or C-H sp³
C 1s 3: C=O
C 1s 4: C=O
C 1s 5: O=C=O
Figure 5.4: High-resolution C 1s peak with fitting after oxygen plasma exposure for (a) 1 s, (b) 3 s, (c) 5 s and (d) 10 s.

The high-resolution Cu 2p spectra of the supporting substrate are shown in Figure 5.5 for various exposure times. The spectra consist mainly of two peaks; one centered around 933 eV and the other one is around 952 eV. No changes are observed before 3 s of exposure, indicating that the graphene film remains continuous and acts as a barrier to oxidation of Cu. However, new peaks form at the shoulders of the existing peaks after 5 and 10 s exposures, accompanied by decrease of the intensity of the main peaks with exposure to oxygen plasma. This indicates that the copper foil becomes exposed to oxidizing species as graphene is itself oxidized and some of it is etched off.

Figure 5.6 shows the variation of the sp² and sp³ contents with plasma exposure time. The results reveal an initial increase of sp² bonding from ~47% in the as-deposited sample up to ~56% after 3 s, followed by a steep drop to 5% after 10 s oxidation. The opposite behavior is observed for the sp³ content, followed by subsequent decrease from ~36% to 23% at 3 s of exposure and an increase up to 70% after 10 s of plasma exposure time.

The decrease of sp² hybridization and relative increase of sp³ hybridization suggests that the latter may be far more resistant to exposure to plasma than the former, which undergoes a combination of oxidation and etching.
Figure 5.5: High-resolution Cu 2p XPS peak for CVD graphene at various exposure times to oxygen plasma.

The almost constant sp\textsuperscript{2} and sp\textsuperscript{3} content indicates the minor effect of oxidation for exposures of 1 s or less. Decrease of sp\textsuperscript{3} content between 1 and 3 s confirms that the initially existing sp\textsuperscript{3} content is not solely due to (C-C) sp\textsuperscript{3}, and can refer to extraction of hydrogen from the surface, thus reducing the (C-H) sp\textsuperscript{3} content resulting in water vapor formation and the synthesis process. This, however, requires further investigation.

Figure 5.6: Variation of sp\textsuperscript{2} and sp\textsuperscript{3} contents with increasing oxygen plasma exposure time.

Plasma oxidation appears to have a destructive effect on the sp\textsuperscript{2} hybridization; as indicated by the increase of sp\textsuperscript{3} hybrids over the sp\textsuperscript{2} ones.
Variation of the overall oxygen content and the various oxide species in the sample with oxidation
time is shown in Figure 5.7. Initial oxygen content of 16% was observed in the as-deposited sample,
mainly in the form of (C-O) and (O=C-O) groups, as can also be seen from Table 5.4. While no
change in overall oxygen content is observed during the first second of exposure, the nature of the
oxide species changes, with (C-O) species increasing at the expense of (O=C-O) species, as shown in
Figure 5.7. Further exposure increases the oxygen content considerably up to ~27% after 5 s
exposure, with the majority of oxygen bonded in (C-O) and (O=C-O) groups. Above 5 s of
exposure, the overall oxygen content decreases to ~23% after 10 s. Such decrease of carbon bonded
oxygen with increased exposure can only be explained by significant loss of carbon from the surface.

The variation of different oxide species is a bit more complicated as shown in Figure 5.7. (C=O)
content stays constant at ~1.6% up to 1 s oxidation, after which it increases to ~5% at 3 s and
decreases again with further exposure. By contrast, (O=C-O) bonds increase continuously with
exposure time greater than 3 s, with a slight decrease observed after 5 s. Both (C-O) and (C=O)
behave in an opposite directions, with (C-O) bonds increasing from 3 – 5 s while (C=O) bonds
decrease. Subsequently, both species decrease with increasing exposure time. The main species
contributing to the overall oxygen content are the epoxide (C-O) and carboxylic (O=C-O) species.

![Figure 5.7: Variation of total oxygen content and oxide species with increasing oxygen plasma exposure time.](image-url)
5.3.4 – Raman spectroscopy

In Figure 5.8, Raman spectra of graphene samples subjected to gradually prolonged exposure to the oxygen plasma are shown. Initial observation reveals D-peak intensity increasing while the 2D-peak intensity decreases with increasing plasma exposure time. The G-peak appears to remain unchanged for all samples except for the appearance and gradual increase in prominence of a side peak at ~1620 cm\(^{-1}\) known as the D’-peak.

Variation of I(D)/I(G) with increasing exposure time to the oxygen plasma is shown in Figure 5.9. The ratio appears to be unaffected for exposures of 1 s or less. It increases abruptly from ~0.14 up to ~2 after 3 s exposure time, followed by slow rise towards an average value of ~2.5 at 10 seconds. The ratio then decreases considerably to ~1 for exposure times of 13s or longer.

The TK equation was used to calculate the mean cluster size of graphene samples from I(D)/I(G) data. The results are summarized numerically in Table 5.5 and plotted with respect to plasma exposure time in Figure 5.10. Graphene clusters size decreases continuously with prolonged plasma exposure, having the most significant decrease at 3 s. It continues decreasing up to 11 s; after which an increase is observed. The decrease in cluster size indicates the effect of ion bombardment on the surface of the sample, which tends to break the graphene sheets into smaller pieces. However, the observed increase indicates that the TK equation is not longer applicable, since the clusters are too
small and the I(D)/I(G) would depend on the probability of the presence of sp\(^3\) clusters rather than the size as explained in section 2.3.2.

Plasma exposure affects the 2D-peak, as seen in Figure 5.8b. In Figure 5.12, the variation of I(2D)/I(G), FWHM and position of the 2D-peak with exposure time to plasma are shown. These figures reveal that most of the changes in 2D-peak parameters occur before 3 s and after 11 s, similar to the behavior of I(D)/I(G) in Figure 5.12. During the first 3 s of plasma exposure, the I(2D)/I(G) decreases from ~2.3 down to 0.8, whereas the 2D peak’s FWHM and position increase from ~36 cm\(^{-1}\) to ~63 cm\(^{-1}\) and from ~2660 cm\(^{-1}\) to ~2680 cm\(^{-1}\), respectively.

![Figure 5.9: Variation of I(D)/I(G) with increasing plasma exposure time.](image)

The initial variation is followed by a period of relative stagnation from 3 to 10 s, during which I(2D)/I(G) decreases slightly from ~0.8 to ~0.5, while the FWHM and the 2D peak position remain unchanged. Further plasma exposure (>10s) results in significant variation in the form of a sharp increase of FWHM to ~200 cm\(^{-1}\) after 13 s and a sharp shift of 2D-peak position to 2720 cm\(^{-1}\). Meanwhile, I(2D)/I(G) decreases slightly to ~0.2.

The G-peak position shown in Figure 5.11 followed a similar trend as the 2D-peak position. A sudden increase is observed from 1568 cm\(^{-1}\) to 1592 cm\(^{-1}\) after 1 s exposure time, followed by a stable regime up to 11 s, then the position shifts towards 1610 cm\(^{-1}\).
The RS results suggest that the structural evolution of graphene with exposure to oxygen plasma occur over three distinct stages. The initial regime sees up to 60% of the changes within 0-3 seconds; the second stage stagnates between 3-11 seconds, showing only a minimal variation and finally a third region from 11 to 15 seconds where important changes are again observed. Another common feature among all the RS parameters is that they almost all follow the same trend during oxygen plasma exposure, except for the I(D)/I(G) which exhibits an opposite trend in the third region.

Table 5.5: Summary of calculated cluster size for various degrees of oxidation.

<table>
<thead>
<tr>
<th>Exposure time (s)</th>
<th>I(D)/I(G)</th>
<th>Cluster size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.13</td>
<td>380</td>
</tr>
<tr>
<td>1</td>
<td>0.14</td>
<td>350</td>
</tr>
<tr>
<td>3</td>
<td>1.99</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>1.83</td>
<td>27</td>
</tr>
<tr>
<td>10</td>
<td>2.36</td>
<td>21</td>
</tr>
<tr>
<td>11</td>
<td>2.48</td>
<td>20</td>
</tr>
<tr>
<td>13</td>
<td>0.81</td>
<td>62</td>
</tr>
<tr>
<td>15</td>
<td>0.84</td>
<td>59</td>
</tr>
</tbody>
</table>

Figure 5.10: Cluster size variation with oxygen plasma exposure time.

Figure 5.11: Variation of G-peak position with oxidation time.
Figure 5.12: Variation of (a) $I(2D)/I(G)$, (b) FWHM and (c) position of the 2D peak with oxygen plasma exposure time.
5.3.5 - Atomic Force Microscopy (AFM)

AFM was performed on graphene-coated copper foil with different plasma exposure times. The macro-scale roughness of the copper foil poses significant difficulties in observing nano-scale features associated to graphene. The quality of images is therefore strongly influenced by the underlying foil.

Nevertheless, AFM topographic and phase images of as-deposited graphene films are shown in Figure 5.13. The images reveal straight lines representing terraces and step edges in the copper foil, as well as some macroparticles representing contamination from the environment. Topographic and phase images of samples oxidized at 3s, 10s and 15s are shown in Figure 5.14, 5.15 and 5.16, respectively. The topography of the surface does not seem to change up to 3 s and appears to be identical to the as-deposited sample. The phase image in Figure 5.14b, as in the case of the as-deposited graphene, reveals abrupt changes in surface properties, corresponding to step edges in the polycrystalline Cu foil. Further exposure of the sample causes the CuO mounds to form over the entire surface. The flat regions, most likely made of partially oxidized graphene now cover the minority of the surface, as seen in Figure 5.16. A close-up view of the surface of the sample exposed for 15 s reveals a triangular sheet of oxidized graphene on Cu foil surface decorated with CuO oxide mounds as shown in Figure 5.17.
In Figure 5.18, topography and phase images for a 3 s plasma oxidized sample are shown. The figure reveals formation of small circular pits in the graphene layer, along with larger regions where graphene is missing.
Figure 5.15: AFM images of graphene sample oxidized for 10 seconds. (a) topographic image and (b) phase image.

Figure 5.16: AFM images of graphene sample oxidized for 15 seconds. (a) topographic image and (b) phase image.
The latter are indicated with black lines and identify regions near large surface corrugations of the copper foil and may correspond to regions with a larger density of grain boundaries which can subsequently undergo preferential etching when exposed to oxygen plasma. The phase image reveals the holes and missing patches of graphene as bright regions.

5.4 – Discussion

Referring back to the three stage model of graphite amorphization trajectory in Figure 2.25 which was suggested by Ferrari, it can be seen that I(D)/I(G) is directly related to disorder in the Graphite \( \rightarrow \) (nc-G) stage, after which the ratio becomes inversely related to the degree of disorder in the (nc-G) \( \rightarrow \) (a-C) stage. This is reflected on the I(D)/I(G) relation to cluster size, which can be estimated using the TK equation. According to this model, increasing disorder occurs by breaking down large graphene domains into nc-G with decreasing cluster size. As the cluster size gets smaller, the TK equation ceases to apply, since the presence of the D-peak would depend on the probability of having such clusters in the sample rather than their actual sizes as described earlier, and
so the I(D)/I(G) starts to decrease with increasing disorder. Considering the I(D)/I(G) data in Figure 5.9 in the context of the three stage model of graphite amorphization, initially graphene undergoes significant breakup of grains resulting into a $G \rightarrow (\text{nc-G})$ transition moving towards stage two. This is confirmed with cluster size calculations shown in Table 5.5 and Figure 5.10, which reveals significant decrease of domain size up to 13 s exposure after which the TK equation doesn’t apply any more.

The initial sudden shifts in Raman parameters up to 3 s can be explained by fast effects of ion bombardment, which can perturb the structure of graphene leading to the various observed changes in the 2D and D-peaks. The stagnant region following the latter implies saturation, after which the (nc-G) film sees appearance of sp$^3$ hybridization, possibly as a result of oxidation.

Carboxylic groups can only form at an edge carbon atom, because carbon is connected to foreign atoms with three of its bonds. The sudden increase in (O=C-O) species after 3 s of exposure according to XPS indicates the formation of new edge sites in the graphene layer. The continuous increase in its content confirms the formation of smaller clusters with a larger edge density, in agreement with RS observations of $G \rightarrow (\text{nc-G})$ transition.

After 10 s of plasma exposure, large hexagonal rings composed of small islands appear on the surface of the foil. These hexagonal features are assumed to be regions of Cu that have oxidized into CuO, resulting in significant volume expansion of up to 77%, as estimated based on bulk molar mass and density values of Cu and CuO. The oxide islands form large hexagonal arrangements because of preferential etching of graphene crystallites from their most vulnerable grain boundaries. This observation is in line with XPS findings that carboxylic groups exclusive to the edges of graphene crystals increase in content and is consistent with appearance of the oxidation peaks in Cu 2p XPS spectra. The formation of smaller graphene crystallites is also consistent with findings from RS.

AFM images, XPS spectra and Raman spectra reveal three main stages of modification of graphene during exposure to oxygen plasma. In the first stage (< 3s), oxygen plasma exposure leads to
structural changes without net uptake of oxygen. AFM reveals no evidence of etching or pit formation in the graphene sheet. However, Raman spectra reveal slight reduction in graphene crystallite size and increased disorder, suggesting some degree of damage and defect formation. Such defects are expected to be uniformly distributed over the surface of graphene, given the nature of ion bombardment, and may become the site of intragrain oxidation during subsequent oxygen plasma exposure. In the second stage (3 s – 10 s), plasma exposure leads to significant uptake of oxygen, formation and significant increase of carboxylic groups, as well as appearance and growth of pits and gaps in the graphene layer, indicating significant etching. This stage is also accompanied by significant oxidation of the supporting Cu foil, as indicated by XPS and AFM. The third stage (> 15 s) is characterized with loss of all sp$^2$ hybridization and corresponds to significant loss of material, as revealed by AFM images. The remaining material shows a very high sp$^3$ character and its oxygen content decreases as well, possibly due to densification and formation of stable diamond like carbon islands.
Chapter VI

Conclusion and Perspectives
6.1 – Conclusion

In this thesis, the structure and composition of two different carbon materials exhibiting very different sp² and sp³ hybridization in planar thin film form have been investigated.

Diamond-like carbon (DLC), an sp³-rich form of carbon, is used extensively in hard drives as corrosion and mechanical wear protection overcoat. The requirements of DLC for magnetic hard drive applications was reviewed, along with the FCVA method, which is proposed as an alternative to depositing ultrathin DLC films via sputtering. DLC films were deposited by this system using a range of deposition angles (50°–90°), deposition times (6 s – 120 s), and biasing conditions (0, -100 V) and investigated by Raman spectroscopy (RS) and X-ray photoelectron spectroscopy (XPS) to explore film structure, namely the sp³ content, which is directly correlated to mechanical properties. Atomic force microscopy (AFM) was used to characterize the surface morphology. The investigation revealed optimum conditions to fabricate smooth DLC films with high sp³ content by FCVA.

As for deposition angle, it was observed that parameters from RS and XPS exhibit different rates of behavior of variation before and after 60°; at which a structural transition is believed to occur in DLC films. RS confirmed that deposition at angles lower than 60° didn’t provide ta-C film, and that such films started to develop afterwards with the largest degree of disorder obtained at 70°. It was concluded that sp³ content as well as sp³/sp² increases continuously with deposition angle as a result of amorphization induced by the more vertical ion bombardment at higher angles. The increase of sp³ hybrids was associated with an increase in roughness as observed from AFM results, until island-like features started to appear on the surface at deposition angles larger than 80°. An optimum deposition angle for DLC films for hard drive applications should provide a smooth film with sufficient mechanical strength, adding more weight to smoothness since a rough surface would conflict with the read/write process of a hard drive. Deposition at 70° is set to be the optimum deposition angle for of DLC films using the custom-made FCVA under study.

Deposition time effect was investigated with RS and AFM, showing that more disordered films and
hence higher sp³ content is associated with longer deposition durations, as a result of elongated ion bombardment on the surface. Roughness was also observed to increase with deposition time as implied by AFM results. However, the results obtained imply that disorder is more dependent on the deposition angle rather than deposition time, and selection of deposition time would be based on controlling the thickness and roughness of obtained films. Based on the study presented in this thesis, a deposition time of 30 seconds is sufficient for the production of smooth and strong DLC films.

Graphene, an sp²-network of carbon atoms, was the subject of the second part of this thesis. CVD graphene on copper foil was exposed to oxygen plasma and the evolution of its structure and chemistry were evaluated by XPS and Raman spectroscopy with respect to exposure time to plasma. Initial characterization of the as-deposited graphene sample indicated a single or bilayer sample having a cluster size of 380 Å as concluded from RS. XPS revealed a sufficient initial sp³ content, which was referred to two main contributions; (1) sp³ hybridized carbon bonding and (2) carbon-hydrogen (C-H) bonding, since both exhibit the same binding energy on the spectrum. The sp³ hybridization is not usually expected in graphene samples deposited by CVD, however, some might have been induced during the high temperature deposition process or the following handling. The presence of carbon-hydrogen content is a reasonable hypothesis since the deposition process included flushing H₂ in the chamber before the introduction of methane. This hypothesis was enforced by the reduction of sp³ content associated with oxygen plasma treatment at initial stages; since it is believed that oxygen species caused removal of hydrogen.

Three distinct stages of structural evolution were observed, beginning with structural modifications, followed by oxidation and etching. Initial exposure to oxygen plasma lead to structural changes without net uptake of oxygen, where some defects are induced by the effect of ion bombardment, and slightly smaller clusters size were observed. The second stage is characterized by increased uptake of oxygen, with breaking of the graphene sheet by the appearance of pits and gaps. This was
supported by the observed increase in carboxylic groups which takes place at edges or grain boundaries of graphene, and the oxidation of the copper foil underneath the graphene sheet. Finally (third stage) significant loss of the material and transformation of sp\(^2\) hybridizations to sp\(^3\) ones as confirmed by XPS and Raman. With such model, a better understanding of graphene oxidation is presented; enabling better control over modification of graphene via oxygen treatment, and offering a tool for developing better reduction methods of GO solutions by indentifying the stage of oxidation and the accompanied oxide species in the sample.

6.2 - Perspectives of this work

The work presented in this thesis provided a gate toward further exploration into two hot areas relating to carbon thin films. The work presented on DLC overcoats was concerned with optimizing the deposition conditions of the custom-made FCVA system without focusing on the film thickness. Future work on this topic should focus on thickness and continuity of DLC films and optimize the deposition parameters accordingly including cross section TEM measurements.

Narrower ranges of angles in between the ones presented should be investigated in future studies, to confirm the concluded trends in this work. Extending the range of angles can also provide a wider idea of what is going on bellow the 50\(^\circ\) deposition angle. The films should be investigated under actual hard drive conditions by deposition on magnetic layers and exposing to actual corrosion and etching conditions.

More investigation should be carried on the initial sp\(^3\) content in as-deposited graphene, since it is not reasonable to have such amount in pure graphite.

The model presented for graphene oxidation is to be investigated more, by introducing more oxidation degrees in between the presented ones, and repeat the same analysis described in this work. Transfer of graphene sheets from the copper foil can improve the topographic imaging of the sheets, besides allowing optical and electrical measurements and the oxidation effect on such properties.
Other sources of oxidation can be used, such as thermal oxidation, and should be compared to the work presented on oxygen plasma treated graphene.

Comparison of the presented oxygen plasma treatment with non-oxidizing (e.g. Ar) plasma, could reveal the effect of ion bombardment and etching of graphene.

The reversible effect of reduction should be explored solely on each stage of oxidation, using different reduction methods presented in literature. Such study can reveal the point at which no further healing in the structure of graphene can be achieved, as well as identifying the optimum reduction methods at each stage.
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